SEMICONDUCTOR ELEMENT, AND

METHOD OF FORMING SILICON-BASED FILM

BACKGROUND OF THE INVENTION

5   Field of the Invention

The present invention relates to a

semiconductor element comprising a semiconductor

junction composed of silicon-based films, and a

method of forming silicon-based films.

10   Related Background Art

When a crystal phase is contained in an i-type

semiconductor layer substantially functioning as an

light-absorbing layer in a photovoltaic element

having a pin junction, a photodegradation phenomenon,

15   which results from a Staebler-Wronski effect and

poses a problem in the case of an amorphous

semiconductor, is advantageously suppressed.

Accordingly, it is effective that the i-type

semiconductor layer contains a crystal phase.

20   Further, a high-mobility TFT is required for a high-

definition and high-luminance liquid crystal panel.

However, a silicon TFT in a crystal phase has a

higher mobility than an amorphous silicon TFT by two

orders or more, so that even if TFT characteristics

25   are substantially improved and the TFT has a

significantly reduced gate width, a current value

required for circuit operations is ensured and a

reduced pixel pitch is obtained compared to amorphous silicon TFTs. Consequently, it becomes relatively easy to reduce the size of the apparatus and increase the definition thereof.

5   Under these circumstances, various attempts have been made for silicon-based thin films containing a crystal phase.

A high-frequency plasma CVD process is one of the excellent methods for enabling silicon-based thin

10   films to be mass-produced partly because this process allows silicon-based thin films larger in area to be formed at low temperature and improves process throughput. Examples of application of silicon-based thin films to products include solar cells and color

15   liquid crystal TFTs, but to popularize these silicon-based films, costs must be further reduced and the performance thereof increased. Thus, establishment of techniques for the high-frequency plasma CVD process is an important technical object.

20   .As a crystal silicon-based thin film layer using a (220) face as a growth face, Japanese Patent Application Laid-Open No. 11-310495 discloses a silicon-based thin film characterized in that the (220) face has a diffraction intensity of 30% or more

25   to the total diffraction intensity.

Further, as an example of an element with a semiconductor layer having a pin junction in which an

i-type semiconductor layer is composed of
microcrystalline silicon, Japanese Patent Application
Laid-Open No. 11-233803 discloses a photovoltaic
element wherein the orientation property of a crystal

5   in the i-type semiconductor layer changes in a depth
direction.

     As described previously, the silicon-based thin
films exhibit excellent characteristics. However,
the former application describes a silicon-based thin

10   film in which the crystal is preferentially oriented
along the (220) face, but does not refer to the
distribution of the orientation property. Further,
the latter application does not refer to a silicon-
based thin film in which the crystal is

15   preferentially oriented along the (220) face.

SUMMARY OF THE INVENTION
     In order to provide a more inexpensive silicon-
based film showing excellent performance, it is an

20   object of the present invention to provide a silicon-
based film having a shortened tact time, an increased
film forming rate, and excellent characteristics, and
a semiconductor element using this silicon-based film
and having excellent adhesion and environmental

25   resistance.

     The present invention provides a semiconductor
element comprising a semiconductor junction composed

of silicon-based films, wherein at least one of the
silicon-based films contains a microcrystal, and the
orientation property of the microcrystal in the
silicon-based film containing the microcrystal

5   changes in a film thickness direction of the silicon-
based film containing the microcrystal.

The present invention provides a semiconductor
element comprising a semiconductor junction composed
of silicon-based films, at least one of the silicon-

10 based films containing a microcrystal, wherein the
silicon-based film containing the microcrystal is
formed by introducing a source gas containing at
least one of a hydrogenated silicon gas and a
fluorinated silicon gas, and hydrogen into a vacuum

15 vessel, introducing high frequency into a high
frequency introducing section in the vacuum vessel,
and using a high frequency plasma process to form a
silicon-based film on a substrate introduced into the
vacuum vessel, wherein heating means for the

20 substrate is arranged opposite a surface of the
substrate on which the silicon-based film containing
the microcrystal is formed, and wherein an output of
the heating means decreases as the silicon-based film
containing the microcrystal is formed.

25 The present invention provides a method of
forming a silicon-based film containing a
microcrystal, comprising forming the film so that the

orientation property of the microcrystal changes in a film thickness direction of the silicon-based film containing the microcrystal.

The present invention provides a method of forming a silicon-based film containing a microcrystal, comprising: introducing a source gas containing at least one of a hydrogenated silicon gas and a fluorinated silicon gas, and hydrogen into a vacuum vessel, introducing high frequency into a high frequency introducing section in the vacuum vessel, and using a high frequency plasma process to form a silicon-based film on a substrate introduced into the vacuum vessel, wherein heating means for the substrate is arranged opposite a surface of the substrate on which the silicon-based film containing the microcrystal is formed, and an output of the heating means decreases as the silicon-based film containing the microcrystal is formed.

Preferably, the semiconductor element is a photovoltaic element including at least one pin type semiconductor junction having a semiconductor layer exhibiting a first conductivity type, i-type semiconductor layers, and a semiconductor layer exhibiting a second conductivity type, the layers being mainly composed of silicon atoms and sequentially stacked on a substrate, wherein at least one of the i-type semiconductor layers includes a

silicon-based film containing a microcrystal, with the orientation property of the microcrystal in the silicon-based film changing in the film thickness direction of the silicon-based film. Preferably, an

5   amorphous silicon layer is arranged between the silicon-based film containing the microcrystal and the semiconductor layer exhibiting the first or second conductivity type which is arranged on a light incidence side relative to the silicon-based film.

10 Preferably, an amorphous silicon layer is arranged between the silicon-based film containing the microcrystal and the semiconductor layer exhibiting the first or second conductivity type. Preferably, the amorphous silicon layer has a film thickness of

15 30 nm or less. Preferably, the orientation property of the microcrystal changes so that the ratio of the diffraction intensity of a (220) face of the microcrystal as which is measured with X rays or electron rays, to the total diffraction intensity .

20 changes in the film thickness direction of the silicon-based film. Preferably, the orientation property of the microcrystal changes so that the ratio of the diffraction intensity of the (220) face of the microcrystal in the silicon-based film

25 containing the microcrystal, which is measured with X rays or electron rays, to the total diffraction intensity is relatively low in an initial stage of

film formation. Preferably, the orientation property
of the microcrystal changes continuously. Preferably,
the silicon-based film containing the microcrystal
includes a region in which the diffraction intensity

5   of the (220) face of the microcrystal, which is
measured with X rays or electron rays, occupies 80%
or more of the total diffraction intensity.
Preferably, in the silicon-based film containing the
microcrystal, the microcrystal which is

10   preferentially oriented along a (110) face is shaped
in a column extending in a vertical direction
relative to the substrate. Preferably, a
microcrystal located in an interface region of the
silicon-based film containing the microcrystal is

15   preferentially oriented along the (100) face.
Preferably, the microcrystal located in the interface
region is shaped in substantially a sphere.
Preferably, the interface region has a film thickness
of 1.0 nm or more and 20 nm or less. Preferably, the

20   silicon-based film containing the microcrystal
contains at least one kind of oxygen atoms, carbon
atoms and nitrogen atoms, and the total amount of the
atoms is 1.5×10^{18} atoms/cm^3 or more and 5.0×10^{19}
atoms/cm^3 or less. Preferably, the silicon-based film

25   containing the microcrystal contains 1.0×10^{19}
atoms/cm^3 or more and 2.5×10^{20} atoms/cm^3 or less of
fluorine atoms. Preferably, the silicon-based film

containing the microcrystal is formed by a high
frequency plasma CVD process of introducing a source
gas containing at least one of a hydrogenated silicon
gas and a fluorinated silicon gas, and hydrogen into

5   a vacuum vessel, introducing high frequency into a
high frequency introducing section in the vacuum
vessel, and forming a silicon-based film on a
substrate introduced into the vacuum vessel.
Preferably, during the process of forming the

10 silicon-based film containing the microcrystal, the
flow rate ratio of the source gas is varied.
Preferably, the source gas is introduced into the
vacuum vessel using a plurality of gas introducing
sections, and the source gas flowing through at least

15 one of the plurality of gas introducing sections has
a flow rate ratio different from that in the other
gas introducing sections. Preferably, the high
frequency is 10 MHz or more and 10 GHz or less.
Preferably, the high frequency is 20 MHz or more and

20 300 MHz or less. Preferably, the distance between
the high frequency introducing section and the
substrate is 3 mm or more and 30 mm or less.
Preferably, the pressure under which the silicon-
based film containing the microcrystal is formed is

25 100 Pa (0.75 Torr) or more and 5,000 Pa (37.5 Torr)
or less. Preferably, a residence time of the source
gas during the formation of the silicon-based film

containing the microcrystal is 0.01 second or more
and 10 seconds or less. Preferably, the residence
time of the source gas during the formation of the
silicon-based film containing the microcrystal is 0.1

5   second or more and 3 seconds or less.

The present invention provides a semiconductor
element comprising a semiconductor junction composed
of silicon-based films, wherein at least one of the
silicon-based films contains a microcrystal, and a

10   microcrystal located in at least one interface region
of the silicon-based films containing the
microcrystal has no orientation property.

Further, the present invention provides a
method of forming a silicon-based film containing a

15   microcrystal, comprising forming the film so that a
microcrystal located in at least one interface region
of the silicon-based films containing the
microcrystal has no orientation property.

Preferably, the semiconductor element is a

20   photovoltaic element including at least one pin type
semiconductor junction having a semiconductor layer
exhibiting a first conductivity type, i-type
semiconductor layers, and a semiconductor layer
exhibiting a second conductivity type, the layers

25   being mainly composed of silicon atoms and
sequentially stacked on a substrate, wherein at least
one of the i-type semiconductor layers includes a

silicon-based film containing a microcrystal, a microcrystal located in at least one interface region of the silicon-based films containing the microcrystal having no orientation property.

5   Preferably, an amorphous silicon layer is arranged between the silicon-based film containing the microcrystal and the semiconductor layer exhibiting the first or second conductivity type which is arranged on a light incidence side relative to the

10   silicon-based film. Preferably, the amorphous silicon layer has a film thickness of 30 nm or less. Preferably, a microcrystal located in at least one of the interface regions has no orientation property, the ratio of the diffraction intensity of a (220)

15   face of the microcrystal except for the non-orientation property region, which is measured with X rays or electron rays, to the total diffraction intensity changes in a film thickness direction of the silicon-based film. Preferably, the orientation

20   property of the microcrystal located in the interface region is such that when measured with X rays or electron rays, three diffraction faces (111), (220), and (311) arranged in this order from the small angle side have such diffraction intensities that when the

25   (111) face has a diffraction intensity of 1, the (220) face has a diffraction intensity of 0.50 or more and 0.60 or less, whereas the (311) face has a

diffraction intensity of 0.25 or more and 0.35 or less. Preferably, the orientation property of the microcrystal changes so that the ratio of the diffraction intensity of the (220) face of the

5 microcrystal in the silicon-based film containing the microcrystal, which is measured by X rays or electron rays, to the total diffraction intensity is relatively low in an initial stage of film formation. Preferably, the orientation property of the

10 microcrystal changes continuously. Preferably, the silicon-based film containing the microcrystal includes a region in which the diffraction intensity of the (220) face of the microcrystal, which is measured with X rays or electron rays, occupies 80%

15 or more of the total diffraction intensity. Preferably, in the silicon-based film containing the microcrystal, a microcrystal which is preferentially oriented along a (110) face is shaped in a column extending in a vertical direction relative to the

20 substrate. Preferably, the microcrystal located in the interface region is shaped in substantially a sphere. Preferably, the interface region has a film thickness of 1.0 nm or more and 20 nm or less. Preferably, the silicon-based film containing the

25 microcrystal contains at least one kind of oxygen atoms, carbon atoms and nitrogen atoms, and the total amount of the atoms is 1.5×10^{18} atoms/cm^3 or more

and 5.0×10^{19} atoms/cm^3 or less. Preferably, the
silicon-based film containing the microcrystal
contains 1.0×10^{19} atoms/cm^3 or more and 2.5×10^{20}
atoms/cm^3 or less of fluorine atoms. Preferably, the

5 silicon-based film containing the microcrystal is
formed by a high frequency plasma CVD process of
introducing a source gas containing at least one of a
hydrogenated silicon gas and a fluorinated silicon
gas, and hydrogen into a vacuum vessel, introducing

10 high frequency into a high frequency introducing
section in the vacuum vessel, and forming a silicon-
based film on a substrate introduced into the vacuum
vessel. Preferably, during the process of forming
the silicon-based film containing the microcrystal,

15 the flow rate ratio of the source gas is varied.
Preferably, the source gas is introduced into the
vacuum vessel using a plurality of gas introducing
sections, and the source gas flowing through at least
one of the plurality of gas introducing sections has

20 a flow rate ratio different from that in the other
gas introducing sections. Preferably, the high
frequency is 10 MHz or more and 10 GHz or less.
Preferably, the high frequency is 20 MHz or more and
300 MHz or less. Preferably, the distance between

25 the high frequency introducing section and the
substrate is 3 mm or more and 30 mm or less.
Preferably, the pressure under which the silicon-

based film containing the microcrystal is formed is
100 Pa (0.75 Torr) or more and 5,000 Pa (37.5 Torr)
or less. Preferably, a residence time of the source
gas during the formation of the silicon-based film

5   containing the microcrystal is 0.01 second or more
and 10 seconds or less. Preferably, the residence
time of the source gas during the formation of the
silicon-based film containing the microcrystal is 0.1
second or more and 3 seconds or less. Preferably,

10   heating means used for the substrate in forming the
silicon-based film containing the microcrystal is
arranged opposite a surface of the substrate on which
the silicon-based film containing the microcrystal is
formed, and an output of the heating means decreases

15   as the silicon-based film containing the microcrystal
is formed.

BRIEF DESCRIPTION OF THE DRAWINGS

       FIG. 1 is a schematic sectional view showing an
20   example of a photovoltaic element including a
semiconductor element according to the present
invention;

       FIG. 2 is a schematic sectional view showing an
example of a deposited film forming apparatus for

25   manufacturing the semiconductor element and
photovoltaic element of the present invention;

       FIG. 3 is a schematic sectional view showing an

example of a semiconductor layer including the
semiconductor element of the present invention;

FIG. 4 is a schematic sectional view showing an
example of a photovoltaic element including the
5   semiconductor element of the present invention;

FIG. 5 is a schematic sectional view showing an
example of a photovoltaic element including the
semiconductor element of the present invention;

FIG. 6 is a schematic sectional view showing an
10 example of a deposited film forming apparatus for
manufacturing the semiconductor element and
photovoltaic element of the present invention;

FIG. 7 is a schematic sectional view showing an
example of a photovoltaic element including the
15 semiconductor element of the present invention; and

FIG. 8 is a schematic sectional view showing an
example of a TFT including the semiconductor element
of the present invention.

20 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

As a result of wholehearted research for
solving the problems described previously, the
inventors have found that a semiconductor element
having good electrical characteristics and excellent
25 adhesion and environmental resistance can be
inexpensively formed by providing a semiconductor
element comprising a semiconductor junction composed

of silicon-based films, at least one of the silicon-based films containing a microcrystal, the element being characterized in that (A) the orientation property of the microcrystal in the silicon-based film containing the microcrystal changes in a film thickness direction or (B) the microcrystal located in at least one of the interface regions of the silicon-based film containing the microcrystal has no orientation property.

The above configuration has the following effects:

Silicon in a crystal phase is characterized in that it has a lower Si-Si bond defect density than silicon in an amorphous phase and a larger carrier mobility and a longer rebinding lifetime than thermodynamically disequilibrium silicon in the amorphous phase. The silicon in the crystal phase is further characterized by having characteristics that are stable over time and which are unlikely to vary in a hot and humid environment or other environments. Thus, for a semiconductor element comprising a semiconductor junction composed of silicon-based films, if a silicon-based film containing a crystal phase is used in, for example, a photovoltaic element or a TFT, then it is possible to form a semiconductor element having excellent characteristics and improved safety.

On the other hand, a problem with the employment of a silicon-based film containing a crystal phase in an i-type semiconductor layer may be degraded performance associated with the adverse

5   effects of crystal boundaries on both majority and minority carriers. To suppress the adverse effects of the crystal boundaries, it may be effective to increase the grain size of the crystal in the i-type semiconductor layer to reduce the density of the

10   crystal boundaries.

Preferred means for increasing the crystal grain size is to suppress the occurrence of crystal nuclei to improve the orientation property of the crystal. If a film is formed in a random crystal

15   orientation, then during growth, crystal grains may collide against each other to relatively reduce their size. However, by directing the crystal in a particular orientation and further controlling the formation of crystal nuclei to make the crystal grow

20   in the same direction, the crystal grains can be restrained from randomly colliding against each other, thereby increasing the crystal grain size. On the other hand, if internal stress occurs in the silicon-based film, a band profile may be distorted, and when

25   the element is irradiated with light, the magnitude of electric fields may decrease in a certain region of a carrier generation layer. Further, for TFTs,

leak current may increase upon switch-off. Thus,
preferably, by changing the orientation property of
the silicon-based film, particularly an interface
region thereof in a film thickness direction during
5 the formation of a deposited film, the internal
stress of the silicon-based film can further be
reduced. The reason why the internal stress is
reduced is that the orientation property can be
changed in the interface region and the internal
10 region of the silicon-based film under different
mechanical stress environments, to change the
directionality of Si-Si bonds.

For crystal silicon having a diamond structure,
a (220) face has the highest atom density, and
15 silicon atoms in the growing outermost face each have
three of its four binding hands combined with other
silicon atoms by covalent binding. Accordingly, if
this is a growth face, a silicon-based film can
preferably be formed in which the microcrystal has
20 good adhesion inside it and to other microcrystals,
and weatherability. Further, if an inverse staggered
TFT is used as the device of an active matrix type
liquid crystal apparatus and if the silicon-based
film containing a microcrystal includes an activated
25 layer having a region which contacts with an Ohmic
contact layer and which is preferentially oriented
along the (220) face, then when the Ohmic contact

layer is dry etched, it can be completely removed
without etching the activated layer or using etching
stopper material such as a nitride film. This is due
to the high etching-resistant property of the (220)

5   face. According to the ASTM card, for crystal
silicon without any orientation, the diffraction
intensity of the (220) face nearly equals 23% of the
sum of the diffraction intensities of 11 reflections
starting with the small angle side, and a structure

10   in which the ratio of the diffraction intensity of
the (220) face exceeds 23% has an orientation
property in this face direction. A structure
including a region where the diffraction intensity of
the (220) face occupies 80% or more of the total

15   diffraction intensity is particularly preferable
because the above effect is promoted.

    As described above, a preferred structure is
such that the orientation property of the
microcrystal contained in the silicon-based film

20   changes in the film thickness direction of the
silicon-based film and that the structure includes a
region where the microcrystal is preferentially
oriented along the (220) face.

    In a pin-type semiconductor junction

25   photovoltaic element having a semiconductor layer
exhibiting a first conductivity type, i-type
semiconductor layers, and a semiconductor layer

exhibiting a second conductivity type, the layers
being sequentially stacked on each other, an
amorphous silicon layer is preferably arranged
between the silicon-based film containing the

5   microcrystal and the semiconductor layer exhibiting
the first or second conductivity type which is
arranged on a light incidence side relative to the
silicon-based film, thereby increasing an open-
circuit voltage. At the same time, a band profile in

10 the vicinity of the interface is improved to prevent
carries from being rebound together, thus allowing
more carriers to be taken out. Furthermore, dopant
atoms from the conductivity type layers are prevented
from diffusing into the i-type semiconductor layers.

15 It may also be preferable to increase the
concentration of hydrogen contained in the amorphous
silicon layer, in the direction of the interface
between this layer and the silicon-based film
containing the microcrystal because this is effective

20 in reducing stress that may occur in the vicinity of
the interface. This is presumably because in a
region with a high hydrogen concentration, a cluster
region containing hydrogen atoms is formed to enhance
the function of absorbing internal stress resulting

25 from the inconsistency between both structures lying
across the interface. In this case, if the amorphous
silicon layer is excessively thick, the

characteristics of the photovoltaic element are affected by degradation of the film caused by light irradiation. Accordingly, the amorphous silicon layer preferably has a film thickness of 30 nm or

5   less.

The method of forming a silicon-based film containing a crystal phase by plasma CVD using high frequency can be carried out in a shorter process time and a lower process temperature in comparison

10   with solid phase reaction. Accordingly, the substrate can be selected from a wider range of alternatives to allow the use of more inexpensive material such as a glass or stainless steel substrate, so that this method is advantageous in reducing costs.

15   In particular, this effect is significant when this method is applied to the i-type semiconductor layers of a photovoltaic element having a pin junction, which layers are thick. In particular, the i-type semiconductor layers are preferably formed at a film

20   forming rate of 2.0 nm/second or more.

In this case, if a silicon-based film with an orientation property is formed by the high frequency plasma CVD process, then the formation occurs in an atmosphere containing activated species contributing

25   to deposition of the silicon-based film as well as activated species contributing to etching. The film deposition progresses while etching the Si-Si bonds

having relatively weak binding force on the surface
of the formed film, thereby forming a silicon-based
film in which the microcrystal is preferentially
oriented along a particular surface. In this case,

5   the orientation property can be controlled by
controlling these activated species.

If such a reaction mechanism is used to form a
film, the crystal having the (220) orientation
property desirably has a low nucleus density in an

10   initial stage of film formation. If the crystal
having the (220) orientation property has a high
nucleus density, a silicon-based film may be formed
using these crystal nuclei as starting points, thus
relatively reducing the size of crystal grains in the

15   entire silicon-based film. Further, if a film is
formed in an atmosphere in which the degree of the
orientation of the interface region increases, i.e.
an atmosphere contributing to etching, then an
underlying layer may be damaged. Thus, in the

20   initial stage of the formation of a silicon-based
film containing a microcrystal, the orientation along
the (220) face is preferably kept relatively
insignificant while ensuring high crystallinity.

If a crystalline silicon-based film is formed,

25   then an amorphous incubation layer with silicon atoms
arranged in disorder may disadvantageously be formed
in the interface region, corresponding to the initial

stage of film formation. This phenomenon occurs

presumably because in the interface region,

corresponding to the initial stage of film formation,

a starting point for film growth has not been

5   clarified yet with the three-dimensional structure of

the atomic arrangement insufficiently established, so

that if the atomic arrangement is disturbed during

film formation, a film is formed while retaining the

disturbed structure therein. In this case, to

10   prevent the above-mentioned amorphous incubation

layer from being formed, it is important to preclude

the atomic arrangement from being disturbed during

the formation of the interface region. If no

hydrogen adheres to the growth face of the silicon

15   with dangling bonds exposed therefrom, then the

symmetry of the atomic arrangement is impaired

because of a Jahn-Teller effect, thereby disturbing

the atomic arrangement to induce the formation of an

amorphous phase. In contrast, if the hydrogen amount

20   present on the growth face exceeds an amount required

to terminate the dangling bonds, then the Si-Si bonds

or Si-H bonds may be cut to reduce the stability of

the structure. These phenomena are particularly

outstanding during high-speed film formation.

25   Thus, the interface region of the silicon-based

film is preferably formed by supplying an appropriate

amount of hydrogen to the growth face in an

atmosphere having a low etching effect. With an
appropriate amount of hydrogen supplied to the growth
face, bonds in the vicinity of the surface are
hardened to reduce the mobility of surface atoms,

5   thereby hindering very small regions formed as buds
of crystal nuclei from joining with adjacent very
small regions having different orientation properties.
Since the buds of the crystal nuclei are not
selectively formed in any particular orientation, the

10   resulting interface region preferably has no
orientation property, i.e. is not oriented along any
particular face. Particularly preferably, in a TFT,
a perfect crystal can be formed in a region
contacting with a gate insulating film, thereby

15   forming a region with high conductivity. To produce
the above effect, the interface region preferably has
a film thickness of 1.0 nm or more and 20 nm or less.

As a result of wholehearted examinations, it
has been found that the orientation property of the

20   interface region is such that when measured with X
rays, three diffraction faces (111), (220), and (311)
arranged in this order from the small angle side have
such diffraction intensities that when the (111) face
has a diffraction intensity of 1, the (220) face has

25   a diffraction intensity of 0.50 or more and 0.60 or
less, whereas the (311) face has a diffraction
intensity of 0.25 or more and 0.35 or less.

Further, in an atmosphere with a relatively small etching effect, the (100) face may grow faster than the (220) face, so that it is possible to reduce the density of crystal nuclei oriented along the (220) face while maintaining excellent crytallinity. Consequently, it is also preferable that the microcrystal in the interface region of the silicon-based film containing the microcrystal is preferentially oriented along the (100) face. In this case, particularly preferably, in a TFT, the region contacting with the gate insulating film can have high conductivity and a very smooth surface. To produce the above effect, the interface region preferably has a film thickness of 1.0 nm or more and 20 nm or less.

Further, to reduce the adhesion and internal stress of the interface, the microcrystal located in the interface region preferably has a substantially spherical outward form having no particular orientation.

The microcrystal in the silicon-based film which is located in a region contiguous to the interface region is preferably more markedly oriented along the (220) face than the interface region using crystal nuclei oriented along the (220) face of the interface region, as seed crystals. In the photovoltaic element, the microcrystal more

preferably has a columnar structure in the direction in which carriers move, thus improving the mobility of the carriers.

Further, when the silicon-based film containing

5   the microcrystal contains at least one kind of oxygen atoms, carbon atoms and nitrogen atoms, the atoms are preferably arranged in void-like spaces at crystal boundaries to improve structural stability. Furthermore, by increasing the resistance of the

10   crystal boundaries, leak current can be suppressed. Moreover, although the reason cannot be explained in detail, the silicon-based film containing the above atoms is preferable because the sectional size of the microcrystal is improved in its uniformity to hinder

15   new crystal nuclei from occurring on the growth face. These effects are more pronounced when the total amount of oxygen, carbon, and nitrogen atoms is 1.5×10^{18} atoms/cm^3 or more. If the total amount of oxygen, carbon, and nitrogen atoms is excessively large, the

20   atoms are incorporated in the bulk of the microcrystal to reduce the crystallinity. The total amount of oxygen, carbon, and nitrogen atoms is preferably 5.0×10^{19} atoms/cm^3 or less.

Further, preferably, when the silicon-based

25   film containing the microcrystal contains fluorine atoms, the microcrystal boundaries are efficiently passivated, and the fluorine atoms, having high

electronegativity, serve to inactivate dangling bonds
of silicon atoms clearly existing at the microcrystal
boundaries. The amount of fluorine atoms is
preferably 1.0×10^{19} atoms/cm^3 or more and 2.5×10^{20}

5   atoms/cm^3 or less.

With a method of introducing a source gas into
a vacuum vessel and using the high frequency plasma
CVD to form a silicon-based film on a substrate
introduced into the vacuum vessel, plasma density per

10 discharge space volume increases with decreasing a
distance between a high frequency introducing section
and the substrate. Accordingly, reaction species
contributing to the formation of a deposited film can
be more densely formed, thereby increasing the film

15 forming rate.

On the other hand, the density of electrons in
plasma and thus the amount of ions generated increase
with decreasing a distance between the high frequency
introducing section and the substrate. Since ions

20 are accelerated by electrostatic attraction in a
sheath region in the discharge space, the resultant
ion collision may distort the arrangement of atoms in
the bulk or form voids in the film, hindering the
formation of a high-quality silicon-based film or

25 degrading adhesion to an underlying layer or
environment resistance. In this case, it is expected
that by increasing a pressure in the film forming

space, the ions in the plasma are more prone to
collide against other ions or activated species to
reduce their impact force or amount, thereby
relatively weakening ion impact.

5   With a high frequency plasma CVD process of
using a source gas containing hydrogenated silicon,
fluorinated silicon and hydrogen, activated species
such as SiF_nH_m ($0 \leq n$, $m \leq 4$), HF, F, H are generated. A
plasma atmosphere containing these activated species

10   is characterized in that some of these species
contribute to deposition of a silicon-based film,
while others contribute to etching. Thus, the film
deposition progresses while etching the Si-Si bonds
having relatively weak binding force in the film

15   surface, thereby making it possible to form a
silicon-based film having higher crystallinity and a
smaller amorphous region. Further, during etching,
as the bonds are cut, radicals are formed to
facilitate structure relaxation, thereby making it

20   possible to form a good silicon-based film at lower
process temperature.

With a high frequency plasma CVD process using
a source gas containing fluorinated silicon and
hydrogen, fluorinated silane-based activated species

25   containing hydrogen such as SiF_2H and $SiFH_2$ which are
formed by adding hydrogen to fluorinated silicon are
formed to enable high-speed film formation. To form

fluorinated silane-based activated species containing
hydrogen such as SiF_2H and $SiFH_2$, it is important to
efficiently decompose fluorinated silicon into SiF
and to achieve an active reaction process using the
formed SiF and activated hydrogen. In particular, it
is important that a sufficient amount of SiF is
present in the plasma.

The control of the plasma process is an
important technical problem in forming a silicon-
based film having the above-described orientation
property and crystallinity, totally at a high film
forming rate by depositing it while carrying out
etching. In this case, it is important to increase
the plasma density per discharge space volume as
described previously in order to achieve an active
reaction process using SiF and activated hydrogen.
However, to form a larger amount of activated
hydrogen in an atmosphere with the density of
electrons in the plasma increased, introduction of
the source gas must be controlled so as to suppress
exhaustion of hydrogen molecules. Furthermore, if
the density of radicals such as SiH and SiH_2
increases in the plasma, crystallization is prone to
occur in the discharge space and on the surface of
the deposited film using these radicals as nuclei.
This may cause reaction by-products such as
polysilane to be formed or inhibit an increase in

crystal grain size, so that the density of radicals

such as SiH and SiH$_2$ must be controlled. To achieve

this, it is effective, while promoting the

decomposition of the source gas, to supply a larger

5   amount of a new source gas to activate secondary

reaction that facilitates elimination of radicals

such as SiH and SiH$_2$ with the source gas

decomposition progressing.

In this connection, as plasma parameters, the

10   volume of the discharge space, in which plasma is

being generated, is defined as V (m^3), the flow rate

of the source gas is defined as Q (cm^3/min (normal)),

and the pressure in the discharge space is defined as

P (Pa). Then, by using a residence time τ(second),

15   defined by $\tau = 592 \times V \times P/Q$, and the luminous

intensity of the plasma as plasma control parameters,

plasma having a desired plasma atmosphere can be

generated. To obtain a high-quality silicon-based

film, it is important to control the residence time

20   in addition to the above-described parameters such as

the distance between the high frequency introducing

section and the substrate, and the pressure.

As a result of wholehearted examinations based

on the above description, the inventors have found

25   that a silicon-based film having a reduced defect

density and excellent characteristics can be formed

at a higher speed in a region in which the residence

time τ, defined by $\tau = 592 \times V \times P/Q$, is 0.01 second

or more and 10 seconds or less when the distance

between the high frequency introducing section and

the substrate is 3 mm or more and 30 mm or less, the

5   pressure in the discharge space is 90 Pa (0.68 Torr)

or more and 1.5×10^4 Pa (113 Torr) or less, the

volume of the discharge space, in which plasma is

being generated, is defined as V (m^3), the flow rate

of the source gas is defined as Q $(cm^3/min (normal))$,

10   and the pressure in the discharge space is defined as

P(Pa). Thus, the density of radicals such as SiH and

SiH_2 can be controlled to form the desired silicon-

based film. In this case, the CVD process preferably

uses a high frequency between 10 MHz and 10 GHz.

15   Furthermore, the CVD process particularly preferably

uses a high frequency between 20 MHz and 300 MHz so

as to appropriately control the temperature of

electrons in the plasma and to form plasma uniformly

extending over a large area.

20   Further, in forming a device such as a

photovoltaic element, the above ranges serve to

suppress degradation of the components, film quality,

and characteristics of the underlying layer due to

reduction effected by hydrogen in the plasma

25   atmosphere, thereby avoiding the adverse effects on

the underlying layer. Using an underlying layer

comprising a transparent conductive film composed of

a metal oxide such as a zinc oxide particularly
effectively prevents a decrease in the transmittance
of the transparent conductive film caused by the
reduction and the associated degradation of the
5 characteristics of the photovoltaic element.

Another effect is improvement of the adhesion
between the silicon-based film and the underlying
layer. This effect is obtained presumably because
the active surface diffusion of SiF_2H and $SiFH_2$
10 radicals causes a deposited film to be formed while
always reducing stress and strain in the vicinity of
the surface. This effect is particularly effective
in a configuration in which the orientation property
in the silicon-based film changes in the film
15 thickness direction. Further, the partial pressure
of the hydrogen relatively increases to enhance the
passivation effect on the crystal boundaries to
further inactivate the crystal boundaries, thereby
suppressing rapid separation of hydrogen atoms
20 incorporated in a silicon network. This prevents a
plastic flow resulting from the occurrence of
irregular regions in the silicon network and
associated cracks or aggregation to enable the
formation of a silicon-based film having high film
25 quality and excellent adhesion. Configuration with
this silicon-based film provides a photovoltaic
element having improved environment resistance.

In view of the adverse effects on the underlying layer and decreases in adhesion, environment resistance, and photodegradation rate, it is preferable that the pressure is 100 Pa (0.75 Torr)

5   or more and 5,000 Pa (37.5 Torr) or less, and the residence time is 0.1 second or more and 3 seconds or less.

By varying the flow rate ratio of gases in the source gas during the formation of a silicon-based

10   film, the ratio of activated species contributing to deposition in the plasma to activated species contributing to etching can be controlled, thereby controlling the orientation property of the microcrystal in the silicon-based film. To form a

15   plasma atmosphere with a high orientation property, conditions can be set such that for a system of fluorinated silicon gas and hydrogen, the partial pressure of the fluorinated silicon gas in the source gas can be increased, or for a system of hydrogenated

20   silicon gas and hydrogen, the partial pressure of the hydrogen in the source gas can be increased, or for a mixed system of fluorinated silicon gas and hydrogenated silicon gas, the partial pressure of the fluorinated silicon gas in the source gas can be

25   increased. The plasma atmosphere can be varied during film deposition by varying the flow rate ratio of the introduced source gas or arranging the

activated species within the plasma so as to obtain a particular distribution of the species density in the case of a film forming method such as a roll-to-roll process in which the substrate is moved in the plasma

5   space. A preferred method is to introduce the source gas into a single plasma space through a plurality of gas introducing sections so that the source gas flowing through at least one of the gas introducing sections has a flow rate ratio different from that in

10   the other gas introducing sections.

To form a silicon-based film containing a crystal phase using the high frequency plasma CVD process, the temperature of the formation surface of the deposited film must be appropriately controlled

15   in order to preferably facilitate reaction processes such as adsorption, separation, removal, injection, and surface diffusion. To achieve this, heating means such as a resistance heater or a lamp heater must be used to directly or indirectly heat the

20   surface of the substrate before forming a silicon-based film containing a crystal phase. On the other hand, induction of plasma increases the temperature of the substrate surface owing to the impact of activated species from the plasma. This is

25   particularly significant if the distance between the high frequency introducing section and the substrate is reduced or high frequency power is raised so as to

increase the plasma density per discharge space volume. If the temperature of the surface of the substrate on which a film is formed becomes excessively high, the reaction processes occurring on

5 the surface are unbalanced, thereby causing crystal nuclei to be formed to increase the density of the crystal boundaries, hindering the film from being appropriately crystallized, or making the inactivation of grain boundaries caused by

10 passivation insufficient. Further, the control of the activated species contributing to film formation is disturbed, thus disordering the control of the orientation property of the crystal phase.

If the temperature of the substrate is

15 controlled using heating means arranged opposite a surface of the substrate on which a silicon-based film containing a microcrystal is formed, then an output of the heating means is preferably reduced while a silicon-based film containing the

20 microcrystal is sequentially formed because the film formed surface is inhibited from being excessively heated. In this connection, for a film forming method such as a roll-to-roll process in which the substrate is moved in the plasma space, outputs of a

25 plurality of heating means arranged in the direction in which the substrate is transported are preferably varied while a deposited film is sequentially formed.

Specifically, a preferred method comprises setting the largest value for the output of the heater located at a position corresponding to the point immediately before the start of film formation and

5 gradually reducing values for the outputs of the heaters following the above heater in the downstream direction of transportation, or zeroing the outputs of at least some of the heaters during film formation.

Now, taking a photovoltaic element as an

10 example of the semiconductor element of the present invention, its components will be described.

FIG. 1 is a schematic sectional view showing an example of the photovoltaic element of the present invention. In the figure, reference numeral 101

15 denotes a substrate, 102 is a semiconductor layer, 103 is a second transparent conductive layer, and 104 is a collecting electrode. Further, reference numeral 101-1 denotes a base member, 101-2 is a metal layer, and 101-3 is a first transparent conductive

20 layer. These members 101-1, 101-2 and 101-3 are the constituent members of the substrate 101.

(Base Member)

Preferably, the base member 101-1 is a plate-like member or a sheet-like member composed of metal,

25 resin, glass, ceramics, or a semiconductor bulk. The surface of the base member may be provided with fine projections and recesses. The base member may be

transparent so that light is incident from the base member side. Alternatively, the base member may be elongate so as to allow a film to be continuously formed using the roll to roll process. In particular, flexible material such as stainless steel or polyimide is suitable as material for the base member 101-1.

(Metal Layer)

The metal layer 101-2 acts as both an electrode and a reflection layer that reflects light reaching the base member 101-1 for reuse in the semiconductor layer 102. A suitable material for the metal layer is Al, Cu, Ag, Au, CuMg, or AlSi. A suitable method of forming the metal layer 101-2 is deposition, sputtering, electrodeposition, or printing. The metal layer 101-2 preferably has an uneven surface. This increases the optical path length of reflected light in the semiconductor layer 102 to increase short circuit current. If the base member 101-1 is conductive, the metal layer 101-2 may not be formed.

(First Transparent Conductive Layer)

The first transparent conductive layer 101-3 serves to boost irregular reflection of incident or reflected light to increase the optical path length in the semiconductor layer 102. Further, the first transparent conductive layer 101-3 serves to prevent elements of the metal layer 101-2 from diffusing or

migrating into the semiconductor layer 102 to shunt the photovoltaic element. Furthermore, when provided with appropriate resistance, the layer 101-3 serves to prevent a short circuit caused by defects such as pinholes in the semiconductor layer. Furthermore, the first transparent conductive layer 101-3 desirably has an uneven surface similarly to the metal layer 101-2. The first transparent conductive layer 101-3 is preferably composed of a conductive oxide such as ZnO or ITO and is preferably formed using a process such as deposition, sputtering, CVD, or electrodeposition. Substance that changes conductivity may be added to these conductive oxides.

Then, an example will be described in which zinc oxide (ZnO) is used as the conductive oxide.

A preferred method of forming a zinc oxide layer is sputtering, electrodeposition, or a combination thereof.

If a zinc oxide film is formed by sputtering, influential conditions include the method used, the type and flow rate of gas, internal pressure, introduced power, film forming rate, and substrate temperature. If for example, a zinc oxide film is formed using a zinc oxide target by DC magnetron sputtering, the type of the gas used includes Ar, Ne, Kr, Xe, Hg, or O_2, and the flow rate, which depends on the size of the apparatus and exhaust velocity, is

desirably between 1 and 100 sccm if for example, the film formation space has a volume of 20 liters. Further, internal pressure during film formation is desirably between 1×10^{-4} and 0.1 Torr. The

5   introduced power, which depends on the size of a target, is desirably between 10 W and 100 KW if the target has a diameter of 15 cm. Further, substrate temperature, the suitable range of which depends on the film forming rate, is desirably between 70°C and

10   450°C if the film forming rate is 1 μm/h.

      To form a zinc oxide film using an electrodeposition process, a water solution containing nitrate and zinc ions is preferably used in a corrosion-resistant vessel. The nitrate and

15   zinc ions desirably have a concentration between 0.001 and 1.0 mol/liter, more desirably between 0.01 and 0.5 mol/liter, and much more desirably between 0.1 and 0.25 mol/liter. A source of nitrate and zinc ions is not particularly limited but may be nitrate

20   zinc, which supplies both ions, or a mixture of water-soluble nitrate such as ammonium nitrate, which supplies nitrate ions, and zinc nitrate, which supplies zinc ions. Furthermore, carbohydrate is preferably added to this water solution in order to

25   suppress abnormal growth and improve the adhesion. The type of carbohydrate is not particularly limited but may be monosaccharide such as glucose (grape

sugar) or fructose (fruit sugar), disaccharide such

as maltose (malt sugar) or saccharose (cane sugar),

polysaccharide such as dextrine or starch, or a

mixture thereof. The amount of carbohydrate in the

5   water solution, which depends on its type, is

desirably between 0.001 and 300 g/liter, more

desirably between 0.005 and 100 g/liter, and much

more desirably between 0.01 and 60 g/liter. If a

zinc oxide film is deposited using the

10   electrodeposition process, then in the water solution

described previously, the base member on which a zinc

oxide film is deposited is used as a negative

electrode, whereas zinc, platinum, or carbon is used

as a positive electrode. In this case, current

15   flowing through a load resistor has a density between

10 mA/dm and 10 A/dm.

(Substrate)

Using the above method, the metal layer 101-2

and the first transparent conductive layer 101-3 are

20   stacked on the base member 101-1 as required to form

a substrate 101. Further, to facilitate integration

of elements, an insulating layer may be provided in

the substrate 101 as an intermediate layer.

(Semiconductor Layer)

25   The semiconductor layer 102, a part of which is

constituted by the silicon-based film of the present

invention, is mainly composed of Si. In addition to

Si, an alloy of Si and C or Ge may be used. For a p-
type, the semiconductor layer contains III group
elements, and for an n-type, it contains V group
elements. As an electrical characteristic of the p-

5   and n-type layers, activation energy is preferably
0.2 eV or less and optimally 0.1 eV or less. Further,
resistivity is preferably 100 Ωcm or less and
optimally 1 Ωcm or less. For a stack cell (a
photovoltaic element having a plurality of pin

10   junctions), preferably the i-type semiconductor layer
of the pin junction closest to the light incidence
side has a wider band gap, and the band gap narrows
as the distance from the light incidence side
increases. A light incidence-side dope layer (p- or

15   n-type) is suitably a crystalline semiconductor with
small light absorption or a semiconductor with a wide
band gap.

The semiconductor layer 102 as a component of
the present invention will be further described. FIG.

20   3 is a schematic sectional view showing the
semiconductor layer 102 having one pin junction as an
example of the photovoltaic element of the present
invention. In this figure, reference numeral 102-1
denotes a semiconductor layer having a first

25   conductivity type, and on the semiconductor layer
102-1 are stacked an i-type semiconductor layer 102-2
composed of the silicon-based film of the present

invention and a semiconductor layer 102-3 exhibiting a second conductivity type. In the semiconductor layer having a plurality of pin junctions, at least one of the pin junctions preferably has the above-

5   described structure.

Further, a stack cell with two pin junctions stacked on each other has a combination of i-type silicon-based semiconductor layers including, for example, an amorphous silicon semiconductor layer and

10   a silicon semiconductor layer containing a microcrystal or a silicon semiconductor layer containing a microcrystal and a silicon semiconductor layer containing a microcrystal arranged in this order from the light incidence side.

15   Furthermore, a stack cell with three pin junctions stacked on each other has a combination of i-type silicon-based semiconductor layers including, for example, an amorphous silicon semiconductor layer, a silicon semiconductor layer containing a

20   microcrystal, and a silicon semiconductor layer containing a microcrystal or an amorphous silicon semiconductor layer, a silicon semiconductor layer containing a microcrystal, and an amorphous silicon germanium semiconductor layer arranged in this order

25   from the light incidence side. The i-type semiconductor layer preferably has an adsorption coefficient (α) of 5,000 cm^{-1} or more of light (630

nm), has a light conductivity (σp) of 10×10^{-5} S/cm
or more when irradiated with solar simulator light
using the solar simulator (AM 1.5, 100 mW/cm^2), and
has a dark conductivity (σd) of 10×10^{-6} S/cm or less

5   and an Urbach energy of 55 meV or less based on a
constant photocurrent method (CPM). The i-type
semiconductor layer may only slightly exhibit p- or
n-type characteristics. Alternatively, if the i-type
semiconductor layer is a silicon germanium

10   semiconductor layer, an i-type semiconductor layer
containing no germanium may be inserted into either a
p/i or n/i interface in order to lower an interface
level and increase open-circuit voltage.
(Method of Forming Semiconductor Layer)

15   The high frequency plasma CVD process is
suitable for forming the silicon-based film and
semiconductor layer 102 of the present invention. A
preferred example of a procedure of forming the
semiconductor layer 102 using the high frequency

20   plasma CVD process will be shown below.

        The internal pressure of a semiconductor
formation vacuum vessel capable of making its inside
in a reduced-pressure state is reduced to a
deposition pressure.

25   Material gases containing a source gas, a
diluting gas and the like are introduced into a
deposition chamber, which is then exhausted using a

vacuum pump so as to set the pressure in the deposition chamber at a predetermined value.

The substrate 101 is set at a predetermined temperature using a heater.

A high frequency oscillated using a high frequency power supply is introduced into the deposition chamber. If the high frequency is a microwave, it is guided into the deposition chamber through a waveguide and via a dielectric window composed of quartz, alumina or aluminum nitride. If the high frequency is VHF or RF, it is guided into the deposition chamber through a coaxial cable and via a metal electrode.

Plasma is induced in the deposition chamber to decompose the source gas to form a deposited film on the substrate 101 arranged in the deposition chamber. This procedure is repeated a plurality of times as required to form the semiconductor layer 102.

As preferred conditions for forming the semiconductor layer 102, the temperature of the substrate in the deposition chamber is from 100 to 450°C, the pressure in the deposition chamber is from 0.067 Pa (0.5 mTorr) to 1.5×10^4 Pa (113 Torr), and high frequency power density is between 0.001 and 2 W/cm^3. Furthermore, to form the silicon-based film of the present invention, the residence time τ, defined by $\tau = 592 \times V \times P/Q$, must be 0.01 second or more and

10 seconds or less when the distance between the high
frequency introducing section and the substrate is 3
mm or more and 30 mm or less, the pressure is 100 Pa
(0.75 Torr) or more and 5,000 Pa (37.5 Torr) or less,

5   the volume of the discharge space, in which plasma is
being generated, is defined as V (m^3), the flow rate
of the source gas is defined as Q (cm^3/min (normal)),
and the pressure in the discharge space is defined as
P(Pa). Further, the high frequency power density is

10   preferably from 0.05 to 2 W/cm^3.

A source gas suitable for forming the silicon-
based film and semiconductor layer 102 of the present
invention includes fluorinated silicon such as SiF_4,
SiH_2F_2, SiH_3F, or Si_2F_6, or a hydrogenated silicon

15   compound such as SiH_4 or Si_2H_6. To obtain an alloy-
based film or layer, a compound such as GeH_4 or CH_4
which contains Ge or C and which can be gasified is
preferably further introduced into the deposition
chamber after being diluted with hydrogen gas.

20   Inactivated gas such as He may further be added.
Further, a compound which contains nitrogen and
oxygen and which can be gasified is may be added as
source gas or diluting gas. A dopant gas for
obtaining a p-type semiconductor layer may be B_2H_6,

25   BF_3, or the like. A dopant gas for obtaining an n-
type semiconductor layer may be PH_3, PF_3, or the like.
To deposit a thin film of a crystal phase or a layer

made of SiC or the like and which has insignificant
light absorption or a large band gap, it is
preferable to increase the ratio of the diluting gas
to the source gas and introduce high frequency with a

5   relatively high power density.

(Second Transparent Conductive Layer)

The second transparent conductive layer 103
serves as a light incidence-side electrode and can
also serve as a reflection preventing film if it has

10   an appropriately set film thickness. The second
transparent conductive layer 103 needs to have a high
transmittance in a wavelength region that can be
absorbed by the semiconductor layer 102 and to have a
low resistivity. The transmittance at 550 nm is

15   preferably 80% or more and more preferably 85% or
more. The resistivity is preferably 5×10^{-3} Ωcm or
less and more preferably 1×10^{-3} Ωcm or less.
Preferred material for the second transparent
conductive layer 103 is ITO, ZnO, In_2O_3, or the like.

20   A preferred method of forming the second transparent
conductive layer 103 is evaporation, CVD, spraying,
spin-on, dipping, or the like. Substance that
changes conductivity may be added to these materials.

(Collecting Electrode)

25   The collecting electrode 104 is provided on the
transparent electrode 103 to improve collecting
efficiency. A preferred method of forming the

collecting electrode 104 is to form metal electrode pattern by sputtering using a mask, or to print conductive paste or solder paste, or to secure a metal wire with conductive paste.

5   Protective layers may be formed on both sides of the photovoltaic element as required. At the same time, a reinforcing material such as a steel plate may be provided on the back surface (at a side opposite to the light incidence side) of the

10   photovoltaic element.

In the following examples, the present invention will be specifically described taking a solar cell and a TFT as examples of semiconductor elements. However, these examples do not limit the

15   contents of the present invention.

[Example 1]

A deposited film forming apparatus 201, shown in FIG. 2, was used to form the photovoltaic element shown in FIG. 4, using the following procedure: FIG.

20   4 is a schematic sectional view showing an example of a photovoltaic element having the silicon-based film of the present invention. In this figure, members that are similar to those in FIG. 1 are denoted by the same reference numerals, and their description is

25   omitted. The semiconductor layer of this photovoltaic element is composed of an amorphous n-type semiconductor layer 102-1A, a microcrystalline

i-type semiconductor layer 102-2A, and a

microcrystalline p-type semiconductor layer 102-3A.

That is, this photovoltaic element is composed of a

so-called pin type single cell.

5   FIG. 2 is a schematic sectional view showing an

example of the deposited film forming apparatus that

manufactures the silicon-based film and photovoltaic

element of the present invention. The deposited film

forming apparatus 201, shown in FIG. 2, is composed

10   of a substrate feeding vessel 202, semiconductor

formation vacuum vessels 211 to 218, and a substrate

wind-up vessel 203 which are all joined together via

gas gates 221 to 229. The deposited film forming

apparatus 201 has a belt-like conductive substrate

15   204 set therein so as to penetrate the vessels and

gas gates. The belt-like conductive substrate 204 is

wound off from a bobbin installed in the substrate

feeding vessel 202 and then wound up around another

bobbin in the substrate wind-up vessel 203.

20   The semiconductor formation vacuum vessels 211

to 218 each have a deposition chamber in which a

plasma induced region is formed. The deposition

chamber is constructed so that a discharge space with

plasma induced therein is vertically defined by the

25   conductive substrate and high frequency introducing

sections and transversely defined by a discharge

plate installed so as to enclose the high frequency

introducing section.

In the plate-like high frequency introducing sections 241 to 248 in the respective deposition chambers, high frequency power supplies 251 to 258

5   apply high frequency power to induce glow discharge, thereby decomposing source gas to deposit a semiconductor layer on the conductive substrate 204. The high frequency introducing sections 241 to 248 are opposite the conductive substrate 204 and each

10   comprise a height adjusting mechanism (not shown in the drawings). The height adjusting mechanisms enable the distance between the conductive substrate and the high frequency introducing sections to be varied, while simultaneously enabling the volume of

15   the discharge space to be varied. Further, the semiconductor formation vacuum vessels 211 to 218 have gas introducing pipes 231 to 238, respectively, connected thereto to introduce a source gas and a diluting gas.

20   The deposited film forming apparatus 201, shown in FIG. 2, comprises eight semiconductor formation vacuum vessels, but in the following examples, glow discharge need not be induced in all the semiconductor formation vacuum vessels. Whether or

25   not glow discharge is induced in a particular vessel can be selected in accordance with the layer configuration of a photovoltaic element to be

manufactured. Further, each semiconductor formation vacuum vessel is provided with a film forming region adjusting plate, not shown in the drawings, for adjusting the contact area between the conductive

5   substrate 204 and discharge space in the deposition chamber.

First, before forming a photovoltaic element, the silicon-based film was experimented and checked for an orientation property. A belt-like base member

10   (50 cm in width, 200 m in length, and 0.125 mm in thickness) composed of stainless steel (SUS430BA) was sufficiently degreased and washed, and then installed in a continuous sputtering apparatus, not shown in the drawings. Then, an Ag electrode was used as a

15   target to deposit a thin Ag film of 100 nm thick on the base member by sputtering. Furthermore, a ZnO target was used to deposit a thin ZnO film of 1.2 μm thick on the thin Ag film by sputtering to form the belt-like conductive substrate 204.

20   Then, a bobbin around which the conductive substrate 204 has been wound was installed in the substrate feeding vessel 202, and the conductive substrate 204 was passed through the loading gas gate, the semiconductor formation vacuum vessels 211, 212,

25   213, 214, 215, 216, 217, and 218, and the unloading gas gate to the substrate wind-up vessel 203, and tension was then adjusted so as not to slacken the

belt-like conductive substrate 204. Then, the
substrate feeding vessel 202, the semiconductor
formation vacuum vessels 211, 212, 213, 214, 215, 216,
217, and 218, and the substrate wind-up vessel 203

5   were sufficiently evacuated down to 6.7×10^{-4} Pa (5 ×
10^{-6} Torr) or less using an evacuation system composed
of a vacuum pump, not shown in the drawings.

Then, a source gas and a diluting gas were
supplied to the semiconductor formation vacuum vessel

10   212 through a gas introducing pipe 232 while
operating the evacuation system. The deposition
chamber in the semiconductor formation vacuum vessel
212 had a longitudinal length of 1 m and a transverse
width of 50 cm. The semiconductor formation vacuum

15   vessels other than the one 212 were supplied with
200-cm^3/min (normal) H_2 gas through gas introducing
pipes, while simultaneously each gas gate was
supplied with 500-cm^3/min (normal) H_2 gas through gate
gas supply pipes (not shown in the drawings) as gate

20   gas. Under these conditions, the exhaust performance
of the evacuation system was adjusted to regulate the
pressure in the semiconductor formation vacuum vessel
212 to a predetermined value. Formation conditions
are shown in the formation conditions for 212 in

25   Table 1.

Once the pressure in the semiconductor
formation vacuum vessel 212 was stabilized, the

conductive substrate 204 started to be moved from the substrate feeding vessel 202 toward the substrate wind-up vessel 203.

Then, high frequency from a high frequency

5   power supply 252 was introduced into the high frequency introducing section 242 in the semiconductor formation vacuum vessel 212, and the height adjusting mechanism was used to set the distance between the conductive substrate and the

10   high frequency introducing section at 9 mm. Glow discharge was induced in the deposition chamber in the semiconductor formation vacuum vessel 212 to form a 1-μm silicon-based film on the conductive substrate 204. At this time, high frequency of 60 MHz was

15   introduced into the semiconductor formation vacuum vessel 212 through the high frequency introducing section 242, composed of a metal electrode made of Al, while adjusting the power density to 400 mW/cm^3 (Comparative Example 1-1).

20   Then, high frequency from a high frequency power supply 253 was introduced into the high frequency introducing section 243 in semiconductor formation vacuum vessel 213, and the height adjusting mechanism was used to set the distance between the

25   conductive substrate and the high frequency introducing section at 9 mm. Glow discharge was induced in the deposition chamber in the

semiconductor formation vacuum vessel 213 to form a
1-μm silicon-based film on the conductive substrate
204. Formation conditions are shown in the formation
conditions for 213 in Table 1. At this time, high

5   frequency of 60 MHz was introduced into the
semiconductor formation vacuum vessel 213 through the
high frequency introducing section 243, composed of a
metal electrode made of Al, while adjusting the power
density to 300 mW/cm^3 (Comparative Example 1-2).

10   When the diffraction peak of each formed
silicon-based film was measured using an X-ray
diffracting apparatus, the silicon-based film of
Comparative Example 1-1 had the highest diffraction
intensity at a (400) face. Further, the (400)

15   diffraction intensity occupied 80% of the sum of the
diffraction intensities of 11 reflections starting
with the smallest angle, indicating that the silicon-
based film of Comparative Example 1-1 was
preferentially oriented along a (100) face.

20   Furthermore, the silicon-based film of Comparative
Example 1-2 had the highest diffraction intensity at
a (220) face, and the (220) diffraction intensity
occupied 90% of the sum of the diffraction
intensities of 11 reflections starting with the

25   smallest angle, indicating that the silicon-based
film of Comparative Example 1-2 was preferentially
oriented along a (110) face.

Then, a photovoltaic element was produced. A source gas and a diluting gas were supplied to the semiconductor formation vacuum vessels 211, 212, 213, and 215 through the gas introducing pipes 231, 232,

5 233, and 235, while operating the evacuation system. The discharge chambers in the semiconductor formation vacuum vessels 212 and 213 each had a longitudinal length of 1 m and a transverse width of 50 cm. Further, the semiconductor formation vacuum vessels

10 other than the ones 211, 212, 213, and 215 were supplied with 200-cm^3/min (normal) H_2 gas through the gas introducing pipes, while simultaneously each gas gate was supplied with 500-cm^3/min (normal) H_2 gas through gate gas supply pipes (not shown in the

15 drawings) as gate gas. Under these conditions, the exhaust performance of the evacuation system was regulated to adjust the pressures in the semiconductor formation vacuum vessels 211, 212, 213, and 215 to predetermined values. Formation

20 conditions are shown in Table 1.

Once the pressures in the semiconductor formation vacuum vessels 211, 212, 213, and 215 were stabilized, the conductive substrate 204 started to be moved from the substrate feeding vessel 202 toward

25 the substrate wind-up vessel 203.

Then, high frequency from the high frequency power supplies 251, 252, 253, and 255 was introduced

into the high frequency introducing sections 241, 242,
243, and 245 in the semiconductor formation vacuum
vessels 211, 212, 213, and 215. Glow discharge was
induced in the deposition chambers in the

5   semiconductor formation vacuum vessels 211, 212, 213,
and 215 to form on the conductive substrate 204 an
amorphous n-type semiconductor layer (film thickness:
30 nm), an i-type semiconductor layer (film
thickness: 1.5 μm), and a microcrystalline p-type

10   semiconductor layer (film thickness: 10 nm), thereby
forming a photovoltaic element. The i-type
semiconductor layer had a total film thickness of 1.5
μm, and the film forming region adjusting plates in
the semiconductor formation vacuum vessels 212 and

15   213 were regulated to adjust the thickness of a
silicon-based film formed in each semiconductor
formation vacuum vessel, as shown in Table 2
(Comparative Example 1-3 and Examples 1-1, 1-2, 1-3,
and 1-4).

20   Then, high frequency power of frequency 13.56
MHz and power density 5 mW/cm^3 was introduced into
the semiconductor formation vacuum vessel 211 through
the high frequency introducing section 241, composed
of a metal electrode made of Al. High frequency was

25   introduced into the semiconductor formation vacuum
vessels 212 and 213 as in the case with the above
described silicon-based films. High frequency power

of frequency 13.56 MHz and power density 30 mW/cm^3 was introduced into the semiconductor formation vacuum vessel 214 through the high frequency introducing section 244, composed of a metal

5   electrode made of Al.

Then, a continuous module forming apparatus, not shown in the drawings, was used to form the formed belt-like photovoltaic elements into solar cell modules of 36 × 22 cm size.

10   The photoelectric conversion efficiencies of the solar cell modules produced as described above were measured using a solar simulator (AM 1.5, 100 mW/cm^2). Further, the adhesion between the conductive substrate and the semiconductor layer was examined

15   using cross cut tape tests (interval between cuts: 1 mm, the number of squares: 100). The results are shown in Table 2.

Furthermore, when the cross section of the photovoltaic element of Example 1-1 was observed

20   using TEM, it was found that in the i-type semiconductor layer, the microcrystal located in a region formed by the semiconductor formation vacuum vessel 212 was spherical and that the microcrystal located in a region formed by the semiconductor

25   formation vacuum vessel 213 was shaped like a column extending vertically relative to the substrate. The surface layer of each i-type semiconductor layer was

preferentially oriented along the (110) face as shown in RHEED figures of samples of the photovoltaic elements, which had been formed up to the i-type semiconductor layer.

5   As is apparent from the above description, solar cell including the semiconductor element of the present invention has excellent characteristics. The characteristics were particularly excellent when a region preferentially oriented along the (100) face

10   had a thickness of 1.0 nm or more and 20 nm or less. [Example 2]

      The deposited film forming apparatus 201, shown in FIG. 2, was used to form the photovoltaic element shown in FIG. 5 using the following procedure: FIG. 5

15   is a schematic sectional view showing an example of a photovoltaic element having the silicon-based film of the present invention. In this figure, members that are similar to those in FIG. 1 are denoted by the same reference numerals, and their description is

20   omitted. The semiconductor layer of this photovoltaic element is composed of an amorphous n-type semiconductor layer 102-1A, a microcrystalline i-type semiconductor layer 102-2A, an amorphous silicon layer 102-10, and a microcrystalline p-type

25   semiconductor layer 102-3A. That is, this photovoltaic element is composed of a so-called pin type single cell.

Then, high frequency from the high frequency
power supplies 251 to 255 was introduced into the
high frequency introducing sections 241 to 245 in the
semiconductor formation vacuum vessels 211 to 215.

5 Glow discharge was induced in the deposition chambers
in the semiconductor formation vacuum vessels 211 to
215 to form on the conductive substrate 204 an
amorphous n-type semiconductor layer (film thickness:
30 nm), a microcrystalline i-type semiconductor layer

10 (film thickness: 1.5 μm), an amorphous silicon layer,
and a microcrystalline p-type semiconductor layer
(film thickness: 10 nm), thereby forming a
photovoltaic element.

The conditions for the interior of the

15 semiconductor formation vacuum vessels 211, 212, 213,
and 215 were similar to those in Example 1-2, and the
conditions for the interior of the semiconductor
formation vacuum vessel 214 are shown in Table 3.
Further, high frequency of 100 MHz was introduced

20 into the semiconductor formation vacuum vessel 214
through the high frequency introducing section 245,
composed of a metal electrode made of Al, while
adjusting the power density to 100 mW/cm^3. Then, the
film forming region adjusting plate in the

25 semiconductor formation vacuum vessel 214 was used to
form photovoltaic elements with the film thicknesses
shown in Table 4. Next, the continuous module

forming apparatus, not shown in the drawings, was used to form the formed belt-like photovoltaic elements into solar cell modules of 36 × 22 cm size (Examples 2-1, 2-2, 2-3, and 2-4).

5   The photoelectric conversion efficiencies of the solar cell modules produced as described above were measured using the solar simulator (AM 1.5, 100 mW/cm^2). Further, the solar cell modules, the initial photoelectric conversion efficiencies of which had

10   previously been measured, were retained at 50°C and then irradiated with solar simulator light of AM 1.5 and 100 mW/cm^2 for 500 hours. Subsequently, the photoelectric conversion efficiencies were measured again to examine changes in photoelectric conversion

15   efficiency associated with the photodegradation test. The results are shown in Table 4.

As is apparent from the above description, solar cells including the semiconductor element of the present invention have excellent characteristics.

20   The characteristics were particularly excellent when the amorphous silicon layer had a thickness of 30 nm or less.

[Example 3]

The deposited film forming apparatus 201, shown

25   in FIG. 2, was used to form the photovoltaic element shown in FIG. 4.

The formation method was similar to that in

Example 1-2 except that SiF$_4$ gas was introduced into the semiconductor formation vacuum vessel 213 together with oxygen the amount of which is shown in Table 5. Then, the continuous module forming apparatus, not shown in the drawings, was used to form the formed belt-like photovoltaic elements into solar cell modules of 36 × 22 cm size (Examples 3-1, 3-2, 3-3, and 3-4).

The photoelectric conversion efficiencies of the solar cell modules produced as described above were measured using the solar simulator (AM 1.5, 100 mW/cm^2). Further, the solar cell modules, the initial photoelectric conversion efficiencies of which had previously been measured, were installed in a dark place at a temperature of 85°C and a humidity of 85% and held there for 30 minutes. Then, 70 minutes were spent reducing the temperature down to -20°C, and then the solar cell modules were held there for 30 minutes. Then, 70 minutes were spent again returning the temperature and humidity to the initial values, i.e. 85°C and 85%. This cycle was repeated 100 times and then the photoelectric conversion efficiencies were measured again to examine changes in photoelectric conversion efficiency associated with the temperature-humidity test. Further, the solar cell modules were subjected to SIMS measurements to evaluate the concentration of oxygen contained in the

silicon-based film formed by the semiconductor formation vacuum vessel 213. The results are shown in Table 6.

Furthermore, when the cross sections of the solar cell modules were observed using TEM, it was found that in the i-type semiconductor layer, the microcrystal located in a region formed by the semiconductor formation vacuum vessel 212 was spherical and that the microcrystal located in a region formed by the semiconductor formation vacuum vessel 213 was shaped like a column extending vertically relative to the substrate. It has been found that the substantially columnar shapes of the solar cell modules of Examples 3-1, 3-2, and 3-3 have a better uniformity in size than those of Examples 1-2 and 3-4.

As is apparent from the above description, solar cells including the semiconductor element of the present invention have excellent characteristics. The characteristics were particularly excellent when the film had an oxygen concentration of 1.5×10^{18} atoms/cm^3 or more and 5.0×10^{19} atoms/cm^3 or less.
[Example 4]

The deposited film forming apparatus 201, shown in FIG. 2, was used to form the photovoltaic element shown in FIG. 4.

The formation method was similar to that in

Example 1-2 except that the source gas shown in Table 7 was introduced into the semiconductor formation vacuum vessel 213. Then, the continuous module forming apparatus, not shown in the drawings, was used to form the formed belt-like photovoltaic elements into solar cell modules of 36 × 22 cm size (Examples 4-1, 4-2, 4-3, 4-4, and 4-5).

The photoelectric conversion efficiencies of the solar cell modules produced as described above were measured using the solar simulator (AM 1.5, 100 mW/cm^2). Further, the solar cell modules, the initial photoelectric conversion efficiencies of which had previously been measured, were installed in a dark place at a temperature of 85°C and a humidity of 85% and held there for 30 minutes. Then, 70 minutes were spent reducing the temperature down to -20°C, and then the solar cell modules were held there for 30 minutes. Then, 70 minutes were spent again returning the temperature and humidity to the initial values, i.e. 85°C and 85%. This cycle was repeated 100 times and then the photoelectric conversion efficiencies were measured again to examine changes in photoelectric conversion efficiency associated with the temperature-humidity test. Further, the solar cell modules were subjected to SIMS measurements to evaluate the concentration of fluorine contained in the silicon-based film formed by the semiconductor

formation vacuum vessel 213. The results are shown in Table 7.

As is apparent from the above description, solar cells including the semiconductor element of the present invention have excellent characteristics. The characteristics were particularly excellent when the film had a fluorine concentration of 1.0×10^{19} atoms/cm^3 or more and 2.5×10^{20} atoms/cm^3 or less.

[Example 5]

The deposited film forming apparatus 201, shown in FIG. 2, was used to form the photovoltaic element shown in FIG. 4.

The formation method was similar to that in Example 2-2 except that, when an i-type semiconductor layer was formed in the semiconductor formation vacuum vessel 213, transportation of the conductive substrate was stopped and the flow rate ratio of gas introduced into the semiconductor formation vacuum vessel 213 was varied as shown in Table 8, while varying the (220) face orientation property so that this orientation becomes gradually large in the film formation direction. In this case, the flow rate of each gas was linearly varied from the start to end of film formation. Then, the continuous module forming apparatus, not shown in the drawings, was used to form the formed belt-like photovoltaic element into a solar cell module of 36 × 22 cm size (Example 5).

The photoelectric conversion efficiency of the solar cell module produced as described above was measured using the solar simulator (AM 1.5, 100 mW/cm^2). It has been found that the solar cell module

5   of Example 5 has a photoelectric conversion efficiency 1.1 times as high as that of Example 2-2.

As is apparent from the above description, solar cells including the semiconductor element of the present invention have excellent characteristics.

10   [Example 6]

The deposited film forming apparatus 201, shown in FIG. 6, was used to form the photovoltaic element shown in FIG. 4.

The formation method was similar to that in

15   Example 2-2 except that two gas introducing pipes (233-1 and 233-2) were connected to the interior of the semiconductor formation vacuum vessel 213, the gas introducing pipe 233-1 was arranged upstream of the gas introducing pipe 232-2 in the direction in

20   which the conductive substrate was transported, while changing the flow rate ratio of the source gas flowing through the gas introducing pipes as shown in Table 9 so that the density of the activated species in the plasma of the semiconductor formation vacuum

25   vessel 213 varies in the direction in which the conductive substrate was transported. The formed belt-like photovoltaic element was formed into a

solar cell module of 36 × 22 cm size (Example 6).

The photoelectric conversion efficiency of the solar cell module produced as described above was measured using the solar simulator (AM 1.5, 100

5   mW/cm^2). It has been found that the solar cell module of Example 6 has a photoelectric conversion efficiency 1.15 times as high as that of Example 2-2.

As is apparent from the above description, solar cells including the semiconductor element of

10   the present invention have excellent characteristics.

[Example 7]

The deposited film forming apparatus 201, shown in FIG. 2, was used to form the photovoltaic element shown in FIG. 4.

15   The formation method was similar to that in Example 2-2 except that the temperature of a lamp heater in the semiconductor formation vacuum vessel 213 was adjusted so that the temperature in the semiconductor formation vacuum vessel 213 was high

20   at the start of film formation (i.e. at an upstream location in the transportation direction) and low at the end of film formation (i.e. at a downstream location in the transportation direction). The formation conditions in the semiconductor formation

25   vacuum vessel 213 are shown in Table 10. The formed belt-like photovoltaic element was formed into a solar cell module of 36 × 22 cm size (Example 7).

The photoelectric conversion efficiency of the solar cell module produced as described above was measured using the solar simulator (AM 1.5, 100 mW/cm^2). It has been found that the solar cell module

5   of Example 7 has a photoelectric conversion efficiency 1.25 times as high as that of Example 2-2.

As is apparent from the above description, solar cells including the semiconductor element of the present invention have excellent characteristics.

10   [Example 8]

The deposited film forming apparatus 201, shown in FIG. 2, was used to form the photovoltaic element shown in FIG. 4.

The formation method was similar to that in

15   Example 2-2 except that the height adjusting mechanisms in the semiconductor formation vacuum vessels 212 and 213 were used to vary the distance between the conductive substrate and the high frequency introducing section as shown in Table 11.

20   The formed belt-like photovoltaic elements were formed into solar cell modules of 36 × 22 cm size.

The photoelectric conversion efficiencies of the solar cell modules produced as described above were measured using the solar simulator (AM 1.5, 100

25   mW/cm^2). The results are shown in Table 10. An i-type semiconductor layer obtained by setting the above distance at 2 mm had a nonuniform thickness and

caused the photoelectric conversion efficiency to significantly vary among the solar cell modules. Solar cell modules obtained by setting the distance between the conductive substrate and the high

5   frequency introducing section at 3 mm or more and 30 mm or less had high photoelectric conversion efficiencies.

As is apparent from the above description, solar cells including the semiconductor element of

10   the present invention have excellent characteristics. [Example 9]

The deposited film forming apparatus 201, shown in FIG. 2, was used to form the photovoltaic element shown in FIG. 4.

15   The formation method was similar to that in Example 2-2 except that the pressure in the semiconductor formation vacuum vessel 213 was varied as shown in Table 12. The formed belt-like photovoltaic elements were formed into solar cell

20   modules of 36 × 22 cm size.

The photoelectric conversion efficiencies of the solar cell modules produced as described above were measured using the solar simulator (AM 1.5, 100 mW/cm^2). Further, the adhesion between the conductive

25   substrate and the semiconductor layer was examined using cross cut tape tests (interval between cuts: 1 mm, the number of squares: 100). Furthermore, the

solar cell modules, the initial photoelectric conversion efficiencies of which had previously been measured, were installed in a dark place at a temperature of 85°C and a humidity of 85% and held

5   there for 30 minutes. Then, 70 minutes were spent reducing the temperature down to -20°C, and then the solar cell modules were held there for 30 minutes. Then, 70 minutes were spent again returning the temperature and humidity to the initial values, i.e.

10 85°C and 85%. This cycle was repeated 100 times and then the photoelectric conversion efficiencies were measured again to examine changes in photoelectric conversion efficiency associated with the temperature-humidity test. The results are shown in

15 Table 12.

Table 12 indicates that solar cell modules including photovoltaic elements produced by setting the pressure in the semiconductor formation vacuum vessel 213 at 90 Pa or more and 15,000 Pa or less

20 have a high photoelectric conversion efficiency and show high performance in peel-off tests and temperature-humidity tests. In particular, solar cell modules including photovoltaic elements produced by setting the pressure at 100 Pa or more and 5,000

25 Pa or less show excellent characteristics in peel-off tests. As is apparent from the above description, solar cell modules including the semiconductor

element of the present invention have excellent

characteristics.

[Example 10]

The deposited film forming apparatus 201, shown

5   in FIG. 2, was used to form the photovoltaic element

shown in FIG. 4.

The formation method was similar to that in

Example 2-2 except that the residence time in

semiconductor formation vacuum vessels 212 and 213

10   was varied as shown in Table 13. The formed belt-

like photovoltaic elements were formed into solar

cell modules of 36 × 22 cm size.

Table 13 indicates that solar cell modules

including photovoltaic elements produced by setting

15   the residence time in the semiconductor formation

vacuum vessel 212 at 0.1 second or more and 10

seconds or less have a high photoelectric conversion

efficiency, show high performance in peel-off tests

and temperature-humidity tests, and have a low

20   photodegradation rate. In particular, solar cell

modules including photovoltaic elements produced by

setting the residence time at 0.2 second or more and

3.0 seconds or less show excellent characteristics in

peel-off tests. As is apparent from the above

25   description, solar cell modules including the

semiconductor element of the present invention have

excellent characteristics.

[Example 11]

The deposited film forming apparatus 201, shown in FIG. 2, was used to form the photovoltaic element shown in FIG. 5 using the following procedure: FIG. 7 is a schematic sectional view showing an example of a photovoltaic element having the silicon-based film of the present invention. In this figure, members that are similar to those in FIG. 1 are denoted by the same reference numerals, and their description is omitted. The semiconductor layer of this photovoltaic element is composed of amorphous n-type semiconductors layers 102-1A and 102-4, the microcrystalline i-type semiconductor layer 102-2A, an amorphous i-type semiconductor layer 102-5, the amorphous silicon layer 102-10, and microcrystalline p-type semiconductor layers 102-3A and 102-6. That is, this photovoltaic element is composed of a so-called pinpin type double cell.

As in Example 1, the belt-like conductive substrate 204 was produced and installed in the deposited film forming apparatus 201, and the substrate feeding vessel 202, the semiconductor formation vacuum vessels 211, 212, 213, 214, 215, 216, 217, and 218, and the substrate wind-up vessel 203 were sufficiently evacuated down to 6.7×10^{-4} Pa (5×10^{-6} Torr) or less using the evacuation system composed of the vacuum pump, not shown in the

drawings.

Then, s source gas and a diluting gas were
supplied to the semiconductor formation vacuum
vessels 211 to 218 through the gas introducing pipes
5   231 to 238 while operating the evacuation system.
The discharge chambers in the semiconductor formation
vacuum vessels 212 and 213 each had a longitudinal
length of 1 m and a transverse width of 50 cm. The
gas gates were supplied with 500-cm^3/min (normal) H_2
10   gas through gate gas supply pipes (not shown in the
drawings) as gate gas. Under these conditions, the
exhaust performance of the evacuation system was
regulated to adjust the pressures in the
semiconductor formation vacuum vessels 211 to 216 to
15   predetermined values. Formation conditions for the
semiconductor formation vacuum vessels 211 to 215
were similar to those in Example 2-2. Formation
conditions for the semiconductor formation vacuum
vessels 216 to 218 are shown in Table 14.

20   Once the pressures in the semiconductor
formation vacuum vessels 211 to 218 were stabilized,
the conductive substrate 204 started to be moved from
the substrate feeding vessel 202 toward the substrate
wind-up vessel 203.

25   Then, high frequency from the high frequency
power supplies 251 to 258 was introduced into the
high frequency introducing sections 241 to 248 in the

semiconductor formation vacuum vessels 211 to 218.
Glow discharge was induced in the deposition chambers
in the semiconductor formation vacuum vessels 211 to
218 to form on the substrate 204 an amorphous n-type

5   semiconductor layer (film thickness: 30 nm), a
microcrystalline i-type semiconductor layer (film
thickness: 2.0 μm), a microcrystalline p-type
semiconductor layer (film thickness: 10 nm), an
amorphous n-type semiconductor layer (film thickness:

10 30 nm), an amorphous i-type semiconductor layer (film
thickness: 300 nm), and a microcrystalline p-type
semiconductor layer (film thickness: 10 nm), thereby
forming a photovoltaic element. A 10-nm thick
microcrystal i-type semiconductor layer was formed in

15 the semiconductor formation vacuum vessel 212. Then,
high frequency power of frequency 13.56 MHz and power
density 5 mW/cm^3 was introduced into the
semiconductor formation vacuum vessels 211 and 216
through the high frequency introducing sections 241

20 and 246, composed of metal electrodes made of Al.
High frequency of 60 MHz was introduced into the
semiconductor formation vacuum vessel 212 through the
high frequency introducing section 242, composed of a
metal electrode made of Al, while adjusting the power

25 density to 400 mW/cm^3. High frequency of 60 MHz was
introduced into the semiconductor formation vacuum
vessel 213 through the high frequency introducing

section 243, composed of a metal electrode made of Al, while adjusting the power density to 300 mW/cm^3. High frequency of 100 MHz was introduced into the semiconductor formation vacuum vessels 214 and 217

5   through the high frequency introducing sections 244 and 247, composed of metal electrodes made of Al, while adjusting the power density to 100 mW/cm^3. High frequency power of frequency 13.56 MHz and power density 30 mW/cm^3 was introduced into the

10   semiconductor formation vacuum vessels 215 and 218 through the high frequency introducing sections 245 and 248, composed of metal electrodes made of Al. Then, the continuous module forming apparatus, not shown in the drawings, was used to form the formed

15   belt-like photovoltaic element into a solar cell module of 36 × 22 cm size.

When the photoelectric conversion efficiency of the solar cell module produced as described above was measured using the solar simulator (AM 1.5, 100

20   mW/cm^2), this solar cell module had a photoelectric conversion efficiency 1.2 times as high as a single solar cell module of Example 2-2. Further, this solar cell module showed high performance in peel-off tests and temperature-humidity tests, indicating that

25   solar cell modules including the semiconductor element of the present invention have excellent characteristics.

[Example 12]

An inverse staggered TFT was formed using the following procedure. FIG. 8 is a schematic sectional view showing an example of an inverse staggered TFT

5 having the semiconductor element of the present invention. As an insulating substrate, a glass substrate 301 is used, on which a gate electrode 302 is formed. Furthermore, on the gate electrode 302 are formed a gate insulating film 303, an activated

10 layer 304 composed of an undoped silicon layer, an Ohmic contact layer 305 arranged in a source-drain region on the activated layer 304 and composed of n^+-type amorphous silicon having a small resistance, and a source-drain electrode 306.

15 First, an Mo-Ta alloy film layer was formed on the glass substrate 301 by a sputtering process and then patterned to form the gate electrode 302. Then, using a CVD process, the gate insulating film 303, composed of a silicon oxide film, was formed.

20 Subsequently, the glass substrate was set in the semiconductor formation vacuum vessel 212 shown in FIG. 2, and then a 15-nm silicon-based film preferentially oriented along the (100) face as in Example 1 was formed. Then, the glass substrate was

25 set in the semiconductor formation vacuum vessel 213, and a 65-nm silicon-based film preferentially oriented along the (110) face as in Example 1 was

formed, thus obtaining the activated layer 304, having a thickness of 80 nm. Then, the glass substrate was set in the semiconductor formation vacuum vessel 211, and the Ohmic contact layer 305,

5   composed of n^+-type amorphous silicon, was deposited and patterned through a lithography process. Furthermore, a metal film was formed and patterned to form the source-drain electrode 306. Finally, a mixed gas of CF_4 and O_2 was used to etch the Ohmic

10 contact layer 305, exposed from the source-drain electrode 306, to form a TFT (Example 12).

A TFT was formed similarly to Example 12 except that the activated layer 304 was formed of an amorphous silicon layer so as to have a thickness of

15 80 nm (Comparative Example 12-1).

A TFT was formed similarly to Example 12 except that the activated layer 304 was formed only of a silicon-based film preferentially oriented along the (100) face, so as to have a thickness of 80 nm

20 (Comparative Example 12-2).

When the Ohmic contact layer 305 was etched, in the TFT of Example 12, the activated layer 304 was not overetched, whereas in the TFTs of the comparative examples, it was overetched, and was thus

25 thinner and had a nonuniform film thickness. In particular, the TFT of Comparative Example 12-1 was significantly overetched. Further, the etching

damage resulted in the formation of a leak path in the activated layer, thus increasing the value of off current compared to Example 12.

   As is apparent from the above description, TFTs including the semiconductor element of the present invention have excellent characteristics.

Table 1

Formation conditions for 211	Source gas	SiH_4: 20 cm^3/min (normal) H_2: 100 cm^3/min (normal) PH_3 (Diluted to 2% with H_2): 30 cm^3/min (normal)
	Substrate temperature	300°C
	Pressure	133 Pa (1.0 Torr)
Formation conditions for 212	Source gas	SiF_4: H_2=10:1 τ=0.3 second
	Substrate temperature	300°C
	Pressure	200 Pa (1.5 Torr)
Formation conditions for 213	Source gas	SiH_4: SiF_4: H_2=1:5:15 τ=0.4 second
	Substrate temperature	350°C
	Pressure	200 Pa (1.5 Torr)
Formation conditions for 215	Source gas	SiH_4: 10 cm^3/min (normal) H_2: 800 cm^3/min (normal) BF_3 (Diluted to 2% with H_2): 100 cm^3/min (normal)
	Substrate temperature	200°C
	Pressure	160 Pa (1.2 Torr)

Table 2

	Comparative Example 1-3	Example 1-1	Example 1-2	Example 1-3	Example 1-4
Thickness of film formed in 212 (nm)	0	1.0	10	20	50
Photoelectric conversion efficiency	1	1.30	1.35	1.32	1.10
Peel-off test	B	AA	AA	AA	A

The photoelectric conversion efficiencies have been standardized by setting the value for Comparative Example 1-3 to 1. For the peel-off tests, the symbols AA, A, B and C indicate that the number of peeled-off squares is 0, 1 to 2, 3 to 10 and 10 to 100, respectively.

Table 3

Formation conditions for 214	Source gas	SiH_4: 200 cm^3/min (normal) H_2: 1000 cm^3/min (normal)
	Substrate temperature	300°C
	Pressure	1000 Pa (7.5 Torr)

Table 4

	Example 2-1	Example 2-2	Example 2-3	Example 2-4
Thickness of film formed in 214 (nm)	0	10	30	50
Photoelectric conversion efficiency	1	1.10	1.15	1.15
Photodegradation rate	1	1.05	1.05	1.20

The photoelectric conversion efficiencies and photodegradation rates have been standardized by setting the value for Comparative Example 2-1 to 1.

Table 5

SiF$_4$ gas (Example 3-1)	SiF$_4$ introduced with 0.1-ppm oxygen
SiF$_4$ gas (Example 3-2)	SiF$_4$ introduced with 0.3-ppm oxygen
SiF$_4$ gas (Example 3-3)	SiF$_4$ introduced with 0.7-ppm oxygen
SiF$_4$ gas (Example 3-4)	SiF$_4$ introduced with 1.0-ppm oxygen

Table 6

	Example 1-2	Example 3-1	Example 3-2	Example 3-3	Example 3-4
Concentration of oxygen in film (atoms/cm^3)	1.0×10^{18}	1.5×10^{18}	7.0×10^{18}	5.0×10^{19}	7.0×10^{19}
Initial photoelectric conversion efficiency	1	1.10	1.15	1.15	1.05
Changes of photoelectric conversion efficiency in temperature-humidity test (Efficiency after test/initial efficiency)	0.95	1.0	1.0	1.0	0.95

Table 7

	Example 4-1	Example 4-2	Example 4-3	Example 4-4	Example 4-5
Source gas for 213 SiH$_4$: SiF$_4$: H$_2$ τ (second)	1:1:15 0.8 sec	1:2:15 0.8 sec	1:3:15 0.8 sec	1:4:15 0.8 sec	1:5:15 0.8 sec
Concentration of fluorine in thin film (atoms/cm^3)	7.5×10^{18}	1.0×10^{19}	8.0×10^{16}	2.5×10^{20}	5.0×10^{20}
Initial photoelectric efficiency	1	1.15	1.20	1.15	1.05
Changes of photoelectric conversion efficiency in temperature-humidity test (Efficiency after test/initial efficiency)	0.95	1.0	1.0	1.0	0.98

Table 8

Formation conditions for 213	Source gas	At start of film formation: SiH_4: SiF_4: H_2=1:3:10, τ=0.4 second At end of film formation: SiH_4: SiF_4: H_2=1:5:15, τ=0.4 second
	Substrate temperature	350°C
	Pressure	200 Pa (1.5 Torr)

Table 9

Formation conditions for 213	Source gas	233-1: SiH_4: SiF_4: H_2=1:3:10 233-2: SiF_4: H_2=1:4 τ=0.4 second
	Substrate temperature	350°C
	Pressure	200 Pa (1.5 Torr)

Table 10

Formation conditions for 213	Source gas	SiH_4: SiF_4: H_2=1:5:15 τ=0.4 second
	Substrate temperature	350°C (at start of film formation) → 250°C (at end of film formation)
	Pressure	200 Pa (1.5 Torr)

Table 11

Distance between conductive substrate and high frequency introducing section (mm)	2	3	6	9	15	30	50
Photoelectric conversion efficiency	−	1	1.05	1.10	1.15	1.10	0.7

The values have been standardized by setting the value obtained when the distance between the conductive substrate and the high frequency introducing section is 3 mm, to 1.

Table 12

Pressure in semiconductor formation vessel 213 (Pa)	50	90	100	1000	5000	10000	15000	20000
Photoelectric conversion efficiency	1	1.25	1.40	1.45	1.50	1.45	1.40	0.9
Peel-off tests	C	A	AA	AA	AA	A	A	B
Temperature-humidity tests	0.70	0.90	1.0	1.0	1.0	0.95	0.9	0.75

The photoelectric conversion efficiencies have been standardized by setting the value obtained when the pressure in the semiconductor formation vacuum vessel 213 is 50 Pa, to 1. For the peel-off tests, the symbols AA, A, B and C indicate that the number of peeled-off squares is 0, 1 to 2, 3 to 10 and 10 to 100, respectively. The results of the temperature-humidity tests show the values of (photoelectric conversion efficiency after the test)/(photoelectric conversion efficiency before the test).

Table 13

Residence time (second) in semiconductor formation vessels 212 and 213	0.008	0.01	0.1	1.0	3.0	10	15
Photoelectric conversion efficiency	1	1.50	1.55	1.60	1.50	1.35	0.80
Peel-off tests	B	A	AA	AA	AA	A	C
Temperature-humidity tests	0.7	0.9	1.0	1.0	1.0	1.0	0.7

The photoelectric conversion efficiencies have been standardized by setting the value obtained when the

residence time in the semiconductor formation vacuum vessels 212 and 213 is 0.008 second, to 1. For the peel-off tests, the symbols AA, A, B and C indicate that the number of peeled-off squares is 0, 1 to 2, 3 to 10 and 10 to 100, respectively. The results of the temperature-humidity tests show the values of (photoelectric conversion efficiency after the test)/(photoelectric conversion efficiency before the test).

Table 14

Formation conditions for 216	Source gas	SiH_4: 20 cm^3/min (normal) H_2: 100 cm^3/min (normal) PH_3 (Diluted to 2% with H_2): 50 cm^3/min (normal)
	Substrate temperature	300°C
	Pressure	133 Pa (1.0 Torr)
Formation conditions for 217	Source gas	SiH_4: 300 cm^3/min (normal) H_2: 4000 cm^3/min (normal)
	Substrate temperature	300°C
	Pressure	1500 Pa (11.3 Torr)
Formation conditions for 218	Source gas	SiH_4: 10 cm^3/min (normal) H_2: 800 cm^3/min (normal) BF_3 (Diluted to 2% with H_2): 100 cm^3/min (normal)
	Substrate temperature	200°C
	Pressure	160 Pa (1.2 Torr)

[Example 13]

The deposited film forming apparatus 201, shown in FIG. 2, was used to form the photovoltaic element shown in FIG. 4, using the following procedure: FIG.

4 is a schematic sectional view showing an example of a photovoltaic element having the silicon-based film of the present invention. In this figure, members that are similar to those in FIG. 1 are denoted by

5 the same reference numerals, and their description is omitted. The semiconductor layer of this photovoltaic element is composed of the amorphous n-type semiconductor layer 102-1A, the microcrystalline i-type semiconductor layer 102-2A, and the

10 microcrystalline p-type semiconductor layer 102-3A. That is, this photovoltaic element is composed of a so-called pin type single cell.

FIG. 2 is a schematic sectional view showing an example of the deposited film forming apparatus that

15 manufactures the silicon-based film and photovoltaic element of the present invention. The deposited film forming apparatus 201, shown in FIG. 2, is composed of the substrate feeding vessel 202, the semiconductor formation vacuum vessels 211 to 218,

20 and the substrate wind-up vessel 203, which are all joined together via the gas gates 221 to 229. The deposited film forming apparatus 201 has the belt-like conductive substrate 204 set therein so as to penetrate the vessels and gas gates. The belt-like

25 conductive substrate 204 is wound off from a bobbin installed in the substrate feeding vessel 202 and then wound up around another bobbin in the substrate

wind-up vessel 203.

The semiconductor formation vacuum vessels 211 to 218 each have a deposition chamber in which a plasma induced region is formed. The deposition

5   chamber is constructed so that a discharge space with plasma induced therein is vertically defined by the conductive substrate and high frequency introducing sections and transversely defined by the discharge plate installed so as to enclose the high frequency

10   introducing section.

In the plate-like high frequency introducing sections 241 to 248 in the respective deposition chambers, high frequency power supplies 251 to 258 apply high frequency power to induce glow discharge,

15   thereby decomposing source gas to deposit a semiconductor layer on the conductive substrate 204. The high frequency introducing sections 241 to 248 are opposite the conductive substrate 204 and each comprise a height adjusting mechanism, not shown in

20   the drawings. The height adjusting mechanisms enable the distance between the conductive substrate and the high frequency introducing sections to be varied, while simultaneously enabling the volume of the discharge space to be varied. Further, the

25   semiconductor formation vacuum vessels 211 to 218 have the gas introducing pipes 231 to 238, respectively, connected thereto to introduce a source

gas and a diluting gas.

The deposited film forming apparatus 201, shown in FIG. 2, comprises eight semiconductor formation vacuum vessels, but in the following examples, glow discharge need not be induced in all the semiconductor formation vacuum vessels. Whether or not glow discharge is induced in a particular vessel can be selected in accordance with the layer configuration of a photovoltaic element to be manufactured. Further, each semiconductor formation vacuum vessel is provided with a film forming region adjusting plate, not shown in the drawings, for adjusting the contact area between the conductive substrate 204 and discharge space in the deposition chamber.

First, before forming a photovoltaic element, the silicon-based film was experimented and checked for an orientation property. A belt-like base member (50 cm in width, 200 m in length, and 0.125 mm in thickness) composed of stainless steel (SUS430BA) was sufficiently degreased and washed, and then installed in the continuous sputtering apparatus, not shown in the drawings. Then, an Ag electrode was used as a target to deposit a thin Ag film of 100 nm thick on the base member by sputtering. Furthermore, a ZnO target was used to deposit a thin ZnO film of 1.2 μm thick on the thin Ag film by sputtering to form the

belt-like conductive substrate 204.

Then, a bobbin around which the conductive substrate 204 had been wound was installed in the substrate feeding vessel 202, and the conductive 5 substrate 204 was passed through the loading gas gate, the semiconductor formation vacuum vessels 211, 212, 213, 214, 215, 216, 217 and 218, and the unloading gas gate to the substrate wind-up vessel 203, and tension was then adjusted so as not to slacken the 10 belt-like conductive substrate 204. Then, the substrate feeding vessel 202, the semiconductor formation vacuum vessels 211, 212, 213, 214, 215, 216, 217 and 218, and the substrate wind-up vessel 203 were sufficiently evacuated down to 6.7×10^{-4} Pa ($5 \times$ 15 10^{-6} Torr) or less using the evacuation system composed of a vacuum pump, not shown in the drawings.

Then, a source gas and a diluting gas were supplied to the semiconductor formation vacuum vessel 212 through the gas introducing pipe 232 while 20 operating the evacuation system. The deposition chamber in the semiconductor formation vacuum vessel 212 had a longitudinal length of 1 m and a transverse width of 50 cm. The semiconductor formation vacuum vessels other than the one 212 were supplied with 25 200-cm^3/min (normal) H_2 gas through gas introducing pipes, while simultaneously each gas gate was supplied with 500-cm^3/min (normal) H_2 gas through the

gate gas supply pipes (not shown in the drawings) as
gate gas. Under these conditions, the exhaust
performance of the evacuation system was regulated to
adjust the pressure in the semiconductor formation

5   vacuum vessel 212 to a predetermined value.
Formation conditions are shown in Sample 15-1 in the
formation conditions for 212 in Table 15.

       Once the pressure in the semiconductor
formation vacuum vessel 212 was stabilized, the

10   conductive substrate 204 started to be moved from the
substrate feeding vessel 202 toward the substrate
wind-up vessel 203.

       Then, high frequency from the high frequency
power supply 252 was introduced into the high

15   frequency introducing section 242 in the
semiconductor formation vacuum vessel 212, and the
height adjusting mechanism was used to set the
distance between the conductive substrate and the
high frequency introducing section at 9 mm. Glow

20   discharge was induced in the deposition chamber in
the semiconductor formation vacuum vessel 212 to form
a 1-μm silicon-based film on the conductive substrate
204. At this time, high frequency of 60 MHz was
introduced into the semiconductor formation vacuum

25   vessel 212 through the high frequency introducing
section 242, composed of a metal electrode made of Al,
while adjusting the power density to 400 mW/cm^3

(Sample 1-1). Silicon-based films were similarly formed while varying the ratio of the source gas (Samples 1-2, 1-3, 1-4 and 1-5).

5 Then, high frequency from a high frequency power supply 253 was introduced into the high frequency introducing section 243 in semiconductor formation vacuum vessel 213, and the height adjusting mechanism was used to set the distance between the conductive substrate and the high frequency

10 introducing section at 9 mm. Glow discharge was induced in the deposition chamber in the semiconductor formation vacuum vessel 213 to form a 1-μm silicon-based film on the conductive substrate 204. Formation conditions are shown in the formation

15 conditions for 213 in Table 3. At this time, high frequency of 60 MHz was introduced into the semiconductor formation vacuum vessel 213 through the high frequency introducing section 243, composed of a metal electrode made of Al, while adjusting the power

20 density to 300 mW/cm^3 (Sample 1-6).

The diffraction peak of each formed silicon-based film was measured using the X-ray diffracting apparatus. The results of measurements of Samples 1-1 to 1-5 are shown in Table 16. Three of these

25 samples, i.e. Samples 1-2, 1-3 and 1-4 had a (220) face diffraction intensity of 0.50 or more and 0.60 or less and a (311) face diffraction intensity of

0.25 or more and 0.35 or less when the diffraction intensity of the (111) face was set to 1.

Further, the silicon-based film of Sample 1-6 had the highest diffraction intensity at the (220)

5   face. Further, the (220) face diffraction intensity occupied 90% of the sum of the diffraction intensities of 11 reflections starting with the smallest angle, indicating that the silicon-based film of Sample 1-6 was preferentially oriented along

10 the (110) face.

Then, a photovoltaic element was produced. A source gas and a diluting gas were supplied to the semiconductor formation vacuum vessels 211, 212, 213 and 215 through the gas introducing pipes 231, 232,

15 233 and 235, while operating the evacuation system. The discharge chambers in the semiconductor formation vacuum vessels 212 and 213 each had a longitudinal length of 1 m and a transverse width of 50 cm. Further, the semiconductor formation vacuum vessels

20 other than the ones 211, 212, 213 and 215 were supplied with 200-cm^3/min (normal) H_2 gas through the gas introducing pipes, while simultaneously each gas gate was supplied with 500-cm^3/min (normal) H_2 gas through gate gas supply pipes (not shown in the

25 drawings) as gate gas. Under these conditions, the exhaust performance of the evacuation system was regulated to adjust the pressures in the

semiconductor formation vacuum vessels 211, 212, 213
and 215 to predetermined values. Photovoltaic
elements were formed by setting the conditions for
the semiconductor formation vacuum vessel 212 in five

5   manners as shown in Table 1. The formation
conditions other than those for the semiconductor
formation vacuum vessel 212 are shown in Table 17.

Once the pressures in the semiconductor
formation vacuum vessels 211, 212, 213 and 215 were

10 stabilized, the conductive substrate 204 started to
be moved from the substrate feeding vessel 202 toward
the substrate wind-up vessel 203.

Then, high frequency from the high frequency
power supplies 251, 252, 253 and 255 was introduced

15 into the high frequency introducing sections 241, 242,
243 and 245 in the semiconductor formation vacuum
vessels 211, 212, 213 and 215. Glow discharge was
induced in the deposition chambers in the
semiconductor formation vacuum vessels 211, 212, 213

20 and 215 to form on the conductive substrate 204 an
amorphous n-type semiconductor layer (film thickness:
30 nm), an i-type semiconductor layer (film
thickness: 1.5 μm), and a microcrystalline p-type
semiconductor layer (film thickness: 10 nm), thereby

25 forming a photovoltaic element. The i-type
semiconductor layer had a total film thickness of 1.5
μm, and the film forming region adjusting plates in

the semiconductor formation vacuum vessels 212 and 213 were regulated to adjust the thickness of a silicon-based film formed in each semiconductor formation vacuum vessel, as shown in Table 18

5   (Comparative Examples 13-1 to 13-9 and Examples 13-1 to 13-12).

Then, high frequency power of frequency 13.56 MHz and power density 5 mW/cm^3 was introduced into the semiconductor formation vacuum vessel 211 through

10   the high frequency introducing section 241, composed of a metal electrode made of Al. High frequency was introduced into the semiconductor formation vacuum vessels 212 and 213 as in the case with the above described silicon-based films. High frequency power

15   of frequency 13.56 MHz and power density 30 mW/cm^3 was introduced into the semiconductor formation vacuum vessel 214 through the high frequency introducing section 244, composed of a metal electrode made of Al.

20   Then, the continuous module forming apparatus, not shown in the drawings, was used to form the formed belt-like photovoltaic elements into solar cell modules of 36 × 22 cm size.

The photoelectric conversion efficiencies of

25   the solar cell modules produced as described above were measured using the solar simulator (AM 1.5, 100 mW/cm^2). Further, the adhesion between the conductive

substrate and the semiconductor layer was examined using cross cut tape tests (interval between cuts: 1 mm, the number of squares: 100). The results are shown in Table 4.

5   Furthermore, when the cross sections of the photovoltaic elements of Examples 13-1 to 13-12 were observed using TEM, it was found that in the i-type semiconductor layer, the microcrystal located in a region formed by the semiconductor formation vacuum

10   vessel 212 was spherical and that the microcrystal located in a region formed by the semiconductor formation vacuum vessel 213 was shaped like a column extending vertically relative to the substrate. The surface layer of each i-type semiconductor layer was

15   preferentially oriented along the (110) face as shown in RHEED figures of samples of the photovoltaic elements, which had been formed up to the i-type semiconductor layer.

As is apparent from the above description,

20   solar cell including the semiconductor element of the present invention has excellent characteristics. The characteristics were particularly excellent when a region without any orientation property had a thickness of 1.0 nm or more and 20 nm or less.

25   [Example 14]

The deposited film forming apparatus 201, shown in FIG. 2, was used to form the photovoltaic element

shown in FIG. 5 using the following procedure: FIG. 5 is a schematic sectional view showing an example of a photovoltaic element having the silicon-based film of the present invention. In this figure, members that

5   are similar to those in FIG. 1 are denoted by the same reference numerals, and their description is omitted. The semiconductor layer of this photovoltaic element is composed of the amorphous n-type semiconductor layer 102-1A, the microcrystalline

10   i-type semiconductor layer 102-2A, the amorphous silicon layer 102-10, and the microcrystalline p-type semiconductor layer 102-3A. That is, this photovoltaic element is composed of a so-called pin type single cell.

15   Then, high frequency from the high frequency power supplies 251 to 255 was introduced into the high frequency introducing sections 241 to 245 in the semiconductor formation vacuum vessels 211 to 215. Glow discharge was induced in the deposition chambers

20   in the semiconductor formation vacuum vessels 211 to 215 to form on the conductive substrate 204 an amorphous n-type semiconductor layer (film thickness: 30 nm), a microcrystalline i-type semiconductor layer (film thickness: 1.5 μm), an amorphous silicon layer,

25   and a microcrystalline p-type semiconductor layer (film thickness: 10 nm), thereby forming a photovoltaic element.

The conditions for the interior of the
semiconductor formation vacuum vessels 211, 212, 213,
and 215 were similar to those in Example 13-2, and
the conditions for the interior of the semiconductor

5   formation vacuum vessel 214 are shown in Table 5.
Further, high frequency of 100 MHz was introduced
into the semiconductor formation vacuum vessel 214
through the high frequency introducing section 245,
composed of a metal electrode made of Al, while

10   adjusting the power density to 100 mW/cm^3. Then, the
film forming region adjusting plate in the
semiconductor formation vacuum vessel 214 was used to
form photovoltaic elements with the film thicknesses
shown in Table 20. Next, the continuous module

15   forming apparatus, not shown in the drawings, was
used to form the formed belt-like photovoltaic
elements into solar cell modules of 36 × 22 cm size
(Examples 14-1, 14-2, 14-3, and 14-4).

The photoelectric conversion efficiencies of

20   the solar cell modules produced as described above
were measured using the solar simulator (AM 1.5, 100
mW/cm^2). Further, the solar cell modules, the initial
photoelectric conversion efficiencies of which had
previously been measured, were retained at 50°C and

25   then irradiated with solar simulator light of AM 1.5
and 100 mW/cm^2 for 500 hours. Subsequently, the
photoelectric conversion efficiencies were measured

again to examine changes in photoelectric conversion efficiency associated with the photodegradation test. The results are shown in Table 20.

As is apparent from the above description,

5   solar cells including the semiconductor element of the present invention have excellent characteristics. The characteristics were particularly excellent when the amorphous silicon layer had a thickness of 30 nm or less.

10 [Example 15]

The deposited film forming apparatus 201, shown in FIG. 2, was used to form the photovoltaic element shown in FIG. 4.

The formation method was similar to that in

15 Example 13-2 except that SiF_4 gas was introduced into the semiconductor formation vacuum vessel 213 together with oxygen the amount of which is shown in Table 7. Then, the continuous module forming apparatus, not shown in the drawings, was used to

20 form the formed belt-like photovoltaic elements into solar cell modules of 36 × 22 cm size (Examples 15-1, 15-2, 15-3 and 15-4).

The photoelectric conversion efficiencies of the solar cell modules produced as described above

25 were measured using the solar simulator (AM 1.5, 100 mW/cm^2). Further, the solar cell modules, the initial photoelectric conversion efficiencies of which had

previously been measured, were installed in a dark place at a temperature of 85°C and a humidity of 85% and held there for 30 minutes. Then, 70 minutes were spent reducing the temperature down to -20°C, and

5   then the solar cell modules were held there for 30 minutes. Then, 70 minutes were spent again returning the temperature and humidity to the initial values, i.e. 85°C and 85%. This cycle was repeated 100 times and then the photoelectric conversion efficiencies

10 were measured again to examine changes in photoelectric conversion efficiency associated with the temperature-humidity test. Further, the solar cell modules were subjected to SIMS measurements to evaluate the concentration of oxygen contained in the

15 silicon-based film formed by the semiconductor formation vacuum vessel 213. The results are shown in Table 22.

Furthermore, when the cross sections of the solar cell modules were observed using TEM, it was

20 found that in the i-type semiconductor layer, the microcrystal located in a region formed by the semiconductor formation vacuum vessel 212 was spherical and that the microcrystal located in a region formed by the semiconductor formation vacuum

25 vessel 213 was shaped like a column extending vertically relative to the substrate. It has been found that the substantially columnar shapes of the

solar cell modules of Examples 15-1, 15-2 and 15-3 have a better uniformity in size than those of Examples 13-2 and 15-4.

5   As is apparent from the above description, solar cells including the semiconductor element of the present invention have excellent characteristics. The characteristics were particularly excellent when the film had an oxygen concentration of 1.5×10^{18} atoms/cm^3 or more and 5.0×10^{19} atoms/cm^3 or less.

10   [Example 16]

The deposited film forming apparatus 201, shown in FIG. 2, was used to form the photovoltaic element shown in FIG. 4.

The formation method was similar to that in

15   Example 13-2 except that the source gas shown in Table 9 was introduced into the semiconductor formation vacuum vessel 213. Then, the continuous module forming apparatus, not shown in the drawings, was used to form the formed belt-like photovoltaic

20   elements into solar cell modules of 36 × 22 cm size (Examples 16-1, 16-2, 16-3, 16-4 and 16-5).

The photoelectric conversion efficiencies of the solar cell modules produced as described above were measured using the solar simulator (AM 1.5, 100

25   mW/cm^2). Further, the solar cell modules, the initial photoelectric conversion efficiencies of which had previously been measured, were installed in a dark

place at a temperature of 85°C and a humidity of 85%
and held there for 30 minutes. Then, 70 minutes were
spent reducing the temperature down to -20°C, and
then the solar cell modules were held there for 30

5   minutes. Then, 70 minutes were spent again returning
the temperature and humidity to the initial values,
i.e. 85°C and 85%. This cycle was repeated 100 times
and then the photoelectric conversion efficiencies
were measured again to examine changes in

10 photoelectric conversion efficiency associated with
the temperature-humidity test. Further, the solar
cell modules were subjected to SIMS measurements to
evaluate the concentration of fluorine contained in
the silicon-based film formed by the semiconductor

15 formation vacuum vessel 213. The results are shown
in Table 23.

As is apparent from the above description,
solar cells including the semiconductor element of
the present invention have excellent characteristics.

20 The characteristics were particularly excellent when
the film had a fluorine concentration of 1.0×10^{19}
atoms/cm^3 or more and 2.5×10^{20} atoms/cm^3 or less.
[Example 17]

The deposited film forming apparatus 201, shown

25 in FIG. 2, was used to form the photovoltaic element
shown in FIG. 4.

The formation method was similar to that in

Example 14-2 except that when an i-type semiconductor layer was formed in the semiconductor formation vacuum vessel 213, transportation of the conductive substrate was stopped and the flow rate ratio of gas

5 introduced into the semiconductor formation vacuum vessel 213 was varied as shown in Table 24, while varying the (220) orientation property so that this orientation becomes gradually large in the film formation direction. In this case, the flow rate of

10 each gas was linearly varied from the start to end of film formation. Then, the continuous module forming apparatus, not shown in the drawings, was used to form the formed belt-like photovoltaic element into a solar cell module of 36 × 22 cm size (Example 17).

15 The photoelectric conversion efficiency of the solar cell module produced as described above was measured using the solar simulator (AM 1.5, 100 mW/cm^2). It has been found that the solar cell module of Example 17 has a photoelectric conversion

20 efficiency 1.15 times as high as that of Example 14-2.

As is apparent from the above description, solar cells including the semiconductor element of the present invention have excellent characteristics.
[Example 18]

25 The deposited film forming apparatus 201, shown in FIG. 6, was used to form the photovoltaic element shown in FIG. 4.

The formation method was similar to that in
Example 14-2 except that the two gas introducing
pipes (233-1 and 233-2) were connected to the
interior of the semiconductor formation vacuum vessel
5   213, the gas introducing pipe 233-1 was arranged
upstream of the gas introducing pipe 233-2 in the
direction in which the conductive substrate was
transported, while changing the flow rate ratio of
the source gas flowing through the gas introducing
10   pipes as shown in Table 25 so that the density of the
activated species in the plasma of the semiconductor
formation vacuum vessel 213 varies in the direction
in which the conductive substrate was transported.
The formed belt-like photovoltaic element was formed
15   into a solar cell module of 36 × 22 cm size (Example
18).

The photoelectric conversion efficiency of the
solar cell module produced as described above was
measured using the solar simulator (AM 1.5, 100
20   mW/cm^2). It has been found that the solar cell module
of Example 18 has a photoelectric conversion
efficiency 1.10 times as high as that of Example 14-2.

As is apparent from the above description,
solar cells including the semiconductor element of
25   the present invention have excellent characteristics.
[Example 19]

The deposited film forming apparatus 201, shown

in FIG. 2, was used to form the photovoltaic element shown in FIG. 4.

The formation method was similar to that in Example 14-2 except that the temperature of the lamp heater in the semiconductor formation vacuum vessel 213 was adjusted so that the temperature in the semiconductor formation vacuum vessel 213 was high at the start of film formation (i.e. at an upstream location in the transportation direction) and low at the end of film formation (i.e. at a downstream location in the transportation direction). The formation conditions in the semiconductor formation vacuum vessel 213 are shown in Table 26. The formed belt-like photovoltaic element was formed into a solar cell module of 36 × 22 cm size (Example 19).

The photoelectric conversion efficiency of the solar cell module produced as described above was measured using the solar simulator (AM 1.5, 100 mW/cm^2). It has been found that the solar cell module of Example 19 has a photoelectric conversion efficiency 1.30 times as high as that of Example 14-2.

As is apparent from the above description, solar cells including the semiconductor element of the present invention have excellent characteristics.

[Example 20]

The deposited film forming apparatus 201, shown in FIG. 2, was used to form the photovoltaic element

shown in FIG. 4.

The formation method was similar to that in Example 14-2 except that the height adjusting mechanisms in the semiconductor formation vacuum

5 vessels 212 and 213 were used to vary the distance between the conductive substrate and the high frequency introducing section as shown in Table 27. The formed belt-like photovoltaic elements were formed into solar cell modules of 36 × 22 cm size.

10 The photoelectric conversion efficiencies of the solar cell modules produced as described above were measured using the solar simulator (AM 1.5, 100 mW/cm^2). The results are shown in Table 27. An i-type semiconductor layer obtained by setting the

15 above distance at 2 mm had a nonuniform thickness and caused the photoelectric conversion efficiency to significantly vary among the solar cell modules. Solar cell modules obtained by setting the distance between the conductive substrate and the high

20 frequency introducing section at 3 mm or more and 30 mm or less had high photoelectric conversion efficiencies.

As is apparent from the above description, solar cells including the semiconductor element of

25 the present invention have excellent characteristics. [Example 21]

The deposited film forming apparatus 201, shown

in FIG. 2, was used to form the photovoltaic element shown in FIG. 4.

The formation method was similar to that in Example 14-2 except that the pressure in the semiconductor formation vacuum vessel 213 was varied as shown in Table 28. The formed belt-like photovoltaic elements were formed into solar cell modules of 36 × 22 cm size.

The photoelectric conversion efficiencies of the solar cell modules produced as described above were measured using the solar simulator (AM 1.5, 100 mW/cm^2). Further, the adhesion between the conductive substrate and the semiconductor layer was examined using cross cut tape tests (interval between cuts: 1 mm, the number of squares: 100). Furthermore, the solar cell modules, the initial photoelectric conversion efficiencies of which had previously been measured, were installed in a dark place at a temperature of 85°C and a humidity of 85% and held there for 30 minutes. Then, 70 minutes were spent reducing the temperature down to -20°C, and then the solar cell modules were held there for 30 minutes. Then, 70 minutes were spent again returning the temperature and humidity to the initial values, i.e. 85°C and 85%. This cycle was repeated 100 times and then the photoelectric conversion efficiencies were measured again to examine changes in photoelectric

conversion efficiency associated with the temperature-humidity test. The results are shown in Table 28.

Table 28 indicates that solar cell modules including photovoltaic elements produced by setting the pressure in the semiconductor formation vacuum vessel 213 at 90 Pa or more and 15,000 Pa or less have a high photoelectric conversion efficiency and show high performance in peel-off tests and temperature-humidity tests. In particular, solar cell modules including photovoltaic elements produced by setting the pressure at 100 Pa or more and 5,000 Pa or less show excellent characteristics in peel-off tests. As is apparent from the above description, solar cell modules including the semiconductor element of the present invention have excellent characteristics.

[Example 22]

The deposited film forming apparatus 201, shown in FIG. 2, was used to form the photovoltaic element shown in FIG. 4.

The formation method was similar to that in Example 14-2 except that the residence time in semiconductor formation vacuum vessels 212 and 213 was varied as shown in Table 29. The formed belt-like photovoltaic elements were formed into solar cell modules of 36 × 22 cm size.

Table 29 indicates that solar cell modules including photovoltaic elements produced by setting the residence time in the semiconductor formation vacuum vessel 212 at 0.1 second or more and 10

5   seconds or less have a high photoelectric conversion efficiency, show high performance in peel-off tests and temperature-humidity tests, and have a low photodegradation rate. In particular, solar cell modules including photovoltaic elements produced by

10   setting the residence time at 0.2 second or more and 3.0 seconds or less show excellent characteristics in peel-off tests. As is apparent from the above description, solar cell modules including the semiconductor element of the present invention have

15   excellent characteristics.
[Example 23]

The deposited film forming apparatus 201, shown in FIG. 2, was used to form the photovoltaic element shown in FIG. 5 using the following procedure: FIG. 7

20   is a schematic sectional view showing an example of a photovoltaic element having the silicon-based film of the present invention. In this figure, members that are similar to those in FIG. 1 are denoted by the same reference numerals, and their description is

25   omitted. The semiconductor layer of this photovoltaic element is composed of the amorphous n-type semiconductors layers 102-1A and 102-4, the

microcrystalline i-type semiconductor layer 102-2A,
the amorphous i-type semiconductor layer 102-5, the
amorphous silicon layer 102-10, and the
microcrystalline p-type semiconductor layers 102-3A

5   and 102-6. That is, this photovoltaic element is
composed of a so-called pinpin type double cell.

As in Example 13, the belt-like conductive
substrate 204 was produced and installed in the
deposited film forming apparatus 201, and the

10 substrate feeding vessel 202, the semiconductor
formation vacuum vessels 211, 212, 213, 214, 215, 216,
217, and 218, and the substrate wind-up vessel 203
were sufficiently evacuated down to 6.7×10^{-4} Pa (5 ×
10^{-6} Torr) or less using the evacuation system

15 composed of the vacuum pump, not shown in the
drawings.

Then, a source gas and a diluting gas were
supplied to the semiconductor formation vacuum
vessels 211 to 218 through the gas introducing pipes

20 231 to 238 while operating the evacuation system.
The discharge chambers in the semiconductor formation
vacuum vessels 212 and 213 each had a longitudinal
length of 1 m and a transverse width of 50 cm. The
gas gates were supplied with 500-cm^3/min (normal) H_2

25 gas through gate gas supply pipes (not shown in the
drawings) as gate gas. Under these conditions, the
exhaust performance of the evacuation system was

regulated to adjust the pressures in the semiconductor formation vacuum vessels 211 to 216 to predetermined values. Formation conditions for the semiconductor formation vacuum vessels 211 to 215

5   were similar to those in Example 14-2. Formation conditions for the semiconductor formation vacuum vessels 216 to 218 are shown in Table 16.

Once the pressures in the semiconductor formation vacuum vessels 211 to 218 were stabilized,

10   the conductive substrate 204 started to be moved from the substrate feeding vessel 202 toward the substrate wind-up vessel 203.

Then, high frequency from the high frequency power supplies 251 to 258 was introduced into the

15   high frequency introducing sections 241 to 248 in the semiconductor formation vacuum vessels 211 to 218. Glow discharge was induced in the deposition chambers in the semiconductor formation vacuum vessels 211 to 218 to form on the conductive substrate 204 an

20   amorphous n-type semiconductor layer (film thickness: 30 nm), a microcrystalline i-type semiconductor layer (film thickness: 2.0 μm), a microcrystalline p-type semiconductor layer (film thickness: 10 nm), an amorphous n-type semiconductor layer (film thickness:

25   30 nm), an amorphous i-type semiconductor layer (film thickness: 300 nm), and a microcrystalline p-type semiconductor layer (film thickness: 10 nm), thereby

forming a photovoltaic element. A 10-nm thick microcrystal i-type semiconductor layer was formed in the semiconductor formation vacuum vessel 212. Then, high frequency power of frequency 13.56 MHz and power

5   density 5 mW/cm^3 was introduced into the semiconductor formation vacuum vessels 211 and 216 through the high frequency introducing sections 241 and 246, composed of metal electrodes made of Al. High frequency of 60 MHz was introduced into the

10   semiconductor formation vacuum vessel 212 through the high frequency introducing section 242, composed of a metal electrode made of Al, while adjusting the power density to 400 mW/cm^3. High frequency of 60 MHz was introduced into the semiconductor formation vacuum

15   vessel 213 through the high frequency introducing section 243, composed of a metal electrode made of Al, while adjusting the power density to 300 mW/cm^3. High frequency of 100 MHz was introduced into the semiconductor formation vacuum vessels 214 and 217

20   through the high frequency introducing sections 244 and 247, composed of metal electrodes made of Al, while adjusting the power density to 100 mW/cm^3. High frequency power of frequency 13.56 MHz and power density 30 mW/cm^3 was introduced into the

25   semiconductor formation vacuum vessels 215 and 218 through the high frequency introducing sections 245 and 248, composed of metal electrodes made of Al.

Then, the continuous module forming apparatus, not
shown in the drawings, was used to form the formed
belt-like photovoltaic element into a solar cell
module of 36 × 22 cm size.

5   When the photoelectric conversion efficiency of
the solar cell module produced as described above was
measured using the solar simulator (AM 1.5, 100
mW/cm^2), this solar cell module had a photoelectric
conversion efficiency 1.2 times as high as a single

10   solar cell module of Example 2-2. Further, this
solar cell module showed high performance in peel-off
tests and temperature-humidity tests, indicating that
solar cell modules including the semiconductor
element of the present invention have excellent

15   characteristics.
[Example 24]

An inverse staggered TFT was formed using the
following procedure. FIG. 8 is a schematic sectional
view showing an example of an inverse staggered TFT

20   having the semiconductor element of the present
invention. As an insulating substrate, the glass
substrate 301 is used, on which the gate electrode
302 is formed. Furthermore, on the gate electrode
302 are formed the gate insulating film 303, the

25   activated layer 304 composed of an undoped silicon
layer, the Ohmic contact layer 305 arranged in a
source-drain region on the activated layer 304 and

composed of n^+-type amorphous silicon having a small resistance, and the source-drain electrode 306.

First, an Mo-Ta alloy film layer was formed on the glass substrate 301 by a sputtering process and then patterned to form the gate electrode 302. Then, using a CVD process, the gate insulating film 303, composed of a silicon oxide film, was formed. Subsequently, the glass substrate was set in the semiconductor formation vacuum vessel 212 shown in FIG. 2, and then a 15-nm silicon-based film without any orientation property was formed under the conditions for Sample 1-3. Then, the glass substrate was set in the semiconductor formation vacuum vessel 213, and a 65-nm silicon-based film preferentially oriented along the (110) face was formed under the conditions for Sample 1-6, thus obtaining the activated layer 304, having a thickness of 80 nm. Then, the glass substrate was set in the semiconductor formation vacuum vessel 211, and the Ohmic contact layer 305, composed of n^+-type amorphous silicon, was deposited and patterned through a lithography process. Furthermore, a metal film was formed and patterned to form the source-drain electrode 306. Finally, a mixed gas of CF_4 and O_2 was used to etch the Ohmic contact layer 305, exposed from the source-drain electrode 306, to form a TFT (Example 24).

A TFT was formed similarly to Example 24 except that the activated layer 304 was formed of an amorphous silicon layer so as to have a thickness of 80 nm (Comparative Example 24-1).

5   A TFT was formed similarly to Example 24 except that the activated layer 304 was formed only of a silicon-based film without any orientation property, so as to have a thickness of 80 nm (Comparative Example 24-2).

10   When the Ohmic contact layer 305 was etched, in the TFT of Example 24, the activated layer 304 was not overetched, whereas in the TFTs of the comparative examples, it was overetched, and was thus thinner and had a nonuniform film thickness. In

15   particular, the TFT of Comparative Example 24-1 was significantly overetched. Further, the etching damage resulted in the formation of a leak path in the activated layer, thus increasing the value of off current compared to Example 24.

20   As is apparent from the above description, TFTs including the semiconductor element of the present invention have excellent characteristics.

As described above, the inventors have found that the present invention enables the inexpensive

25   formation of a semiconductor element having good electrical characteristics and excellent adhesion and environment resistance.

Table 15

Formation conditions for 212	Source gas	(Sample 1-1) SiH_4: SiF_4: H_2=2:1:10 τ=0.3 second
		(Sample 1-2) SiH_4: SiF_4: H_2=2:2:10 τ=0.3 second
		(Sample 1-3) SiH_4: SiF_4: H_2=2:3:10 τ=0.4 second
		(Sample 1-4) SiH_4: SiF_4: H_2=2:4:10 τ=0.4 second
		(Sample 1-5) SiH_4: SiF_4: H_2=2:5:10 τ=0.4 second
	Substrate temperature	300°C
	Pressure	200 Pa (1.5 Torr)

Table 16

Sample	(111) diffraction intensity	(220) diffraction intensity	(311) diffraction intensity
Sample 1-1	1	0.45	0.40
Sample 1-2	1	0.50	0.35
Sample 1-3	1	0.52	0.31
Sample 1-4	1	0.60	0.25
Sample 1-5	1	0.65	0.10

Table 17

Formation conditions for 211	Source gas	SiH_4: 20 cm^3/min (normal) H_2: 100 cm^3/min (normal) PH_3 (Diluted to 2% with H_2): 30 cm^3/min (normal)
	Substrate temperature	300°C
	Pressure	133 Pa (1.0 Torr)
Formation conditions for 213	Source gas	SiH_4: SiF_4: H_2=1:5:15 τ=0.4 second
	Substrate temperature	350°C
	Pressure	200 Pa (1.5 Torr)
Formation conditions for 215	Source gas	SiH_4: 10 cm^3/min (normal) H_2: 800 cm^3/min (normal) BF_3 (Diluted to 2% with H_2): 100 cm^3/min (normal)
	Substrate temperature	200°C
	Pressure	160 Pa (1.2 Torr)

Table 18

	Formation conditions in 212	Film thickness in 212 (nm)	Photoelectric conversion efficiency	Peel-off tests
Comparative Example 13-1	Sample 1	0	1	B
Comparative Example 13-2	Sample 1	1.0	1.01	B
Comparative Example 13-3	Sample 1	10	1.02	B
Comparative Example 13-4	Sample 1	20	1.03	B
Comparative Example 13-5	Sample 1	50	1.00	B
Example 13-1	Sample 2	1.0	1.30	AA
Example 13-2	Sample 2	10	1.35	AA
Example 13-3	Sample 2	20	1.30	AA
Example 13-4	Sample 2	50	1.25	A
Example 13-5	Sample 3	1.0	1.32	AA
Example 13-6	Sample 3	10	1.35	AA
Example 13-7	Sample 3	20	1.33	AA
Example 13-8	Sample 3	50	1.30	A
Example 13-9	Sample 4	1.0	1.34	AA
Example 13-10	Sample 4	10	1.33	AA
Example 13-11	Sample 4	20	1.35	AA
Example 13-12	Sample 4	50	1.30	A
Comparative Example 13-6	Sample 5	1.0	1.02	B
Comparative Example 13-7	Sample 5	10	1.05	B
Comparative Example 13-8	Sample 5	20	1.04	B
Comparative Example 13-9	Sample 5	50	1.02	B

The photoelectric conversion efficiencies have been standardized by setting the value for Comparative Example 13-1 to 1. For the peel-off tests, the symbols AA, A, B and C indicate that the number of peeled-off squares is 0, 1 to 2, 3 to 10 and 10 to 100, respectively.

Table 19

Formation conditions for 214	Source gas	SiH$_4$: 200 cm^3/min (normal) H$_2$: 1000 cm^3/min (normal)
	Substrate temperature	300°C
	Pressure	1000 Pa (7.5 Torr)

Table 20

	Example 14-1	Example 14-2	Example 14-3	Example 14-4
Thickness of film formed in 214 (nm)	0	10	30	50
Photoelectric conversion efficiency	1	1.12	1.17	1.15
Photodegradation rate	1	1.03	1.02	1.20

The photoelectric conversion efficiencies and photodegradation rates have been standardized by setting the value for Example 14-1 to 1.

Table 21

SiF$_4$ Gas (Example 15-1)	SiF$_4$ introduced with 0.1-ppm oxygen
SiF$_4$ Gas (Example 15-2)	SiF$_4$ introduced with 0.3-ppm oxygen
SiF$_4$ Gas (Example 15-3)	SiF$_4$ introduced with 0.7-ppm oxygen
SiF$_4$ Gas (Example 15-4)	SiF$_4$ introduced with 1.0-ppm oxygen

Table 22

	Example 13-2	Example 15-1	Example 15-2	Example 15-3	Example 15-4
Concentration of oxygen in film (atoms/cm^3)	1.0×10^{18}	1.5×10^{18}	7.0×10^{18}	5.0×10^{19}	7.0×10^{19}
Initial photoelectric conversion efficiency	1	1.12	1.13	1.15	1.05
Changes of photoelectric conversion efficiency in temperature-humidity test (Efficiency after test/initial efficiency)	0.98	1.0	1.0	1.0	0.95

Table 23

	Example 16-1	Example 16-2	Example 16-3	Example 16-4	Example 16-5
Source gas for 213 SiH$_4$: SiF$_4$: H$_2$ τ (second)	1:1:15 0.8 sec	1:2:15 0.8 sec	1:3:15 0.8 sec	1:4:15 0.8 sec	1:5:15 0.8 sec
Concentration of fluorine in thin film (atoms/cm^3)	7.5×10^{18}	1.0×10^{19}	8.0×10^{16}	2.5×10^{20}	5.0×10^{20}
Initial photoelectric efficiency	1	1.15	1.20	1.15	1.05
Changes of photoelectric conversion efficiency in temperature-humidity test (Efficiency after test/initial efficiency)	0.95	1.0	1.0	1.0	0.98

Table 24

Formation conditions for 213	Source gas	At start of film formation: SiH_4: SiF_4: H_2=1:3:10, τ=0.4 second At end of film formation: SiH_4: SiF_4: H_2=1:5:15, τ=0.4 second
	Substrate temperature	350°C
	Pressure	200 Pa (1.5 Torr)

Table 25

Formation conditions for 213	Source gas	233-1: SiH_4: SiF_4: H_2=1:3:10 233-2: SiF_4: H_2=1:4 τ=0.4 second
	Substrate temperature	350°C
	Pressure	200 Pa (1.5 Torr)

Table 26

Formation conditions for 213	Source gas	SiH_4: SiF_4: H_2=1:5:15 τ=0.4 second
	Substrate temperature	350°C (at start of film formation) → 250°C (at end of film formation)
	Pressure	200 Pa (1.5 Torr)

Table 27

Distance between conductive substrate and high frequency introducing section (mm)	2	3	6	9	15	30	50
Photoelectric conversion efficiency	–	1	1.03	1.07	1.10	1.10	0.7

The values have been standardized by setting the value obtained when the distance between the conductive substrate and the high frequency introducing section is 3 mm, to 1.

Table 28

Pressure in semiconductor formation vessel 213 (Pa)	50	90	100	1000	5000	10000	15000	20000
Photoelectric conversion efficiency	1	1.20	1.38	1.42	1.50	1.45	1.35	0.9
Peel-off tests	C	A	AA	AA	AA	A	A	B
Temperature-humidity tests	0.70	0.90	1.0	1.0	1.0	0.95	0.9	0.75

The photoelectric conversion efficiencies have been standardized by setting the value obtained when the pressure in the semiconductor formation vacuum vessel 213 is 50 Pa, to 1. For the peel-off tests, the symbols AA, A, B and C indicate that the number of peeled-off squares is 0, 1 to 2, 3 to 10 and 10 to 100, respectively. The results of the temperature-humidity tests show the values of (photoelectric conversion efficiency after the test)/(photoelectric conversion efficiency before the test).

Table 29

Residence time (second) in semiconductor formation vessels 212 and 213	0.008	0.01	0.1	1.0	3.0	10	15
Photoelectric conversion efficiency	1	1.45	1.50	1.60	1.55	1.35	0.80
Peel-off tests	B	A	AA	AA	AA	A	C
Temperature-humidity tests	0.7	0.9	1.0	1.0	1.0	1.0	0.7

The photoelectric conversion efficiencies have been standardized by setting the value obtained when the

residence time in the semiconductor formation vacuum

vessels 212 and 213 is 0.008 second, to 1. For the

peel-off tests, the symbols AA, A, B and C indicate

that the number of peeled-off squares is 0, 1 to 2, 3

5   to 10 and 10 to 100, respectively. The results of

the temperature-humidity tests show the values of

(photoelectric conversion efficiency after the

test)/(photoelectric conversion efficiency before the

test).

10

Table 30

Formation conditions for 216	Source gas	SiH$_4$: 20 cm^3/min (normal) H$_2$: 100 cm^3/min (normal) PH$_3$ (Diluted to 2% with H$_2$): 50 cm^3/min (normal)
	Substrate temperature	300°C
	Pressure	133 Pa (1.0 Torr)
Formation conditions for 217	Source gas	SiH$_4$: 300 cm^3/min (normal) H$_2$: 4000 cm^3/min (normal)
	Substrate temperature	300°C
	Pressure	1500 Pa (11.3 Torr)
Formation conditions for 218	Source gas	SiH$_4$: 10 cm^3/min (normal) H$_2$: 800 cm^3/min (normal) BF$_3$ (Diluted to 2% with H$_2$): 100 cm^3/min (normal)
	Substrate temperature	200°C
	Pressure	160 Pa (1.2 Torr)